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THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*Aluminium Alcohols.* Part I. *Their Preparation by Means of the Aluminium-Iodine Reaction.*

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.C.S., Lecturer on Chemistry in Dulwich College.

In a communication made to this Society in 1876, **29**, p. 158 of this Journal, we stated that aluminium or aluminium iodide singly is without action on absolute alcohol, but that together they decompose the liquid with facility. The resulting bodies are hydrogen and two new organic aluminic compounds, aluminic iodo-ethylate, $(C_2H_5O)_3I_3Al_2$, and aluminic ethylate, $Al_2(C_2H_5O)_6$. We showed too that the metallic iodide and the metal need not exist together in equivalent proportions, in order either to initiate or to continue this decomposition, and in fact that one molecule of the iodide suffices to bring about the combination of very many atoms of aluminium with the oxy-radical of the alcohol.* We also showed that the amount of hydrogen set free is equivalent to that of the metal which disappears, and is quite independent of the quantity of iodide present.

With regard to the part which this salt plays, two views were enunciated. The one for which we expressed a preference supposed that the reaction takes place through the intervention of intermediate bodies, thus:—

(*a*.) $3(C_2H_5O.H) + Al_2I_6 = Al_2(C_2H_5O)_3I_3 + 3HI.$

(*b*.) $Al_2(C_2H_5O)_3I_3 + 3(C_2H_5O.H) = Al_2(C_2H_5O)_6 + 3HI.$

(*c*.) $6HI + Al_2 = Al_2I_6 + 3H_2.$

* We have since obtained the combination of as much as 54 atoms of aluminium by means of one molecule of the iodide.

It will be understood that the complete conversion of the aluminic iodide into the iodo-ethylate, and this again into the ethylate, as by equations *a* and *b*, occurs only when the freed hydriodic acid is destroyed, as by equation *c*.

Whether, however, this be the true view, was not decided by our experiments. And it appears from both the suppositions referred to, that a relatively small quantity of the iodide should bring about the decomposition of an unlimited quantity of alcohol in presence of the metal. Such, it is evident, would be the case were it not for the mechanical interference of the solid products of the reaction.

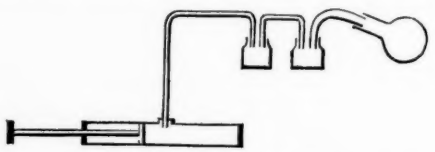
In the present communication, we establish more completely our knowledge of the composition and properties of the ethylate, and describe the results obtained on applying the *aluminium-iodine reaction* (*Proc. Roy. Soc.*, 1880, 546) to the preparation of analogous aluminium derivatives of other alcohols.

General Instructions.

Into a flask, fitted with an inverted condenser, place the alcohol, aluminium, and iodine in the proportions of 20* c.c. of the liquid, 2 grams of the metal, and 1 gram of iodine, and heat the substances by immersing the bulb of the vessel in boiling water. The elements quickly combine and produce the necessary aluminic iodide, and the decomposition of the alcohol begins before the whole of the free iodine passes into combination; and proceeds moderately rapidly until the metal disappears and the evolution of hydrogen stops. The contents of the flask are now heated to about 300° in an oil-bath, and continued at this temperature until distillation practically ends. The distillate consists of the excess of alcohol used, mixed generally with some of its iodide, which latter compound results from the decomposition in presence of alcohol of the intermediate iodo-body, very probably in accordance with the equation:

$$Al_2(C_nH_{2n+1}O)_3I_3 = Al_2O_3 + 3C_nH_{2n+1}I.$$

The flask is next attached to a receiver by means of a piece of short wide tubing, this receiver to another, and the second to a pump. The general arrangement is shown in the figure.



* With alcohols of high molecular weight, it is necessary to increase this volume to 30 or 40 c.c., and to heat to a higher temperature than 100° C.

The apparatus is now exhausted of air, the product in the flask melted and then heated till distillation is over, the pump being kept at work during the operation. Some of the distillate usually passes into the second receiver, but the greater part always collects in the first. Even when the vacuum is kept as perfect as possible some decomposition always occurs, the amount of which varies for the different compounds, as will be shown hereafter. Of the alcohols already isolated in this way, the ethylate distils with the greatest, and the amylate with the least facility.

The aluminium used was in the form of foil, cut into small pieces, and of such a thickness that 1 gram measured 110 square centimetres.

University of

Aluminic Methylate.

We have stated in the paper to which reference has already been made, that methyl alcohol is not affected when boiled with aluminium and aluminium iodide. We find, however, that this liquid suffers some amount of decomposition when the iodide is formed in the boiling alcohol, but only while iodine remains in a free condition; further, that when the metal is conjoined with platinum deposited from the chloride, the decomposition of the alcohol continues long after the whole of the iodine has passed into combination.

In an experiment employing 2 grams of aluminium coated with platinum, 2 grams of iodine, and 20 c.c. of methyl alcohol, 800 c.c. of hydrogen were set free in three hours, on heating to the boiling point of the liquid. The atomic ratio of aluminium to iodine found in the residue was 1 to 0·62; and after 18 hours' heating, when the action was proceeding extremely slowly, 1 : 0·4. These numbers, and the knowledge of what takes place under practically analogous circumstances with other alcohols of the same series, enable the composition to be assigned to the solid product of this reaction with a considerable degree of probability. Calculating the iodine as iodo-compound, and the aluminium as methylate, and subtracting from this latter the methylate corresponding to the iodo-compound, 100 parts of the solid products when the experiment was stopped, would appear to consist of 55·6 parts of aluminic methylate, and 44·4 parts of aluminic iodo-methylate. Attempts made to separate these compounds were not successful, owing probably to the unstable character of the methylate.

Aluminic Ethylate.

We supplement the directions which have already been published for the preparation of this compound, by giving the details of an experiment, following the plan described under the heading "general instructions."

2 grams of iodine, 4 grams of aluminium, and 40 c.c. of alcohol were heated as directed. The first litre of hydrogen collected in 5 minutes, the second in 4, the third in 10, the fourth in 16 minutes. Evolution of gas continued for 10 more minutes. The total hydrogen collected measured 4,345 c.c. (corrected). The product in the flask was solid, and on heating at 300°, and then *in vacuo*, gave 12·5 grams of distillate quite free from iodide.

Several quantities of the substance collected as described were found on analysis to contain from 1—2 per cent. of aluminium in excess of that which ethylate would require. This discrepancy we thought might very probably arise from decomposition of the distillate while in the receivers. The first estimation of aluminium was made in a part of the last portion of distillate collected in the upper part of the tubule of an ordinary condenser, the analytical details of which we now subjoin, and also the results of the analysis of two other specimens, which were collected in small quantities in cooled receivers, the object of this being to induce rapid solidification, and to minimise the influence of the diminished pressure.

I. 1·062 gram dissolved in dilute nitric acid, and aluminium precipitated by ammonia and ignited, gave 0·330 gram Al_2O_3.

II. 0·4465 gram of a different preparation, treated with water to decompose it, dried at 100° and ignited, gave 0·146 Al_2O_3.

III. 0·272 gram burnt with oxygen and oxide of copper gave 0·4395 gram CO_2 and 0·2385 gram H_2O.

		Calculated.	Found. I.	Found. II.	Found. III.
Al_2	55	16·92	16·58	17·46	—
C_{12}	144	44·30	—	—	44·06
H_{30}	30	9·23	—	—	9·74
O_6	96	29·55	—	—	—
$Al_2(C_2H_5O)_6$ ..	325	100·00			

Considering the difficulties attending the purification, these analytical numbers accord sufficiently well with those calculable on the supposition that the body examined has an atomic composition agreeing with the formula $Al(C_2H_5O)_3$, and from analogy the molecular formula $Al_2(C_2H_5O)_6$. Such a compound receives the name of aluminic ethylate, it being evidently an analogue of Williamson's potassium and sodium ethylates.

Aluminic Propylate.

Normal propyl alcohol boils, according to Chancel, at 96—97°; to Rossi, at 96°; and to Pierre and Puchot, at 98·5°. The alcohol used for the experiments about to be described boiled at 96°.

2 grams of aluminium, 1 gram of iodine, and 20 c.c. of the alcohol were heated to 100°. The first litre of gas collected in 18 minutes, and the second litre in 33 minutes. The action slowly continued for 15 more minutes. The total hydrogen evolved measured 2,145 c.c. (corr.). On heating the residue to 300°, considerable frothing was noticed, and a non-fusible substance was left in the flask. This was found to be free from iodine, and gave on treatment with water and ignition 61 per cent. of alumina. From this it would appear to consist in 100 parts, of 52·1 parts of aluminic propylate and 47·9 of alumina, showing that some 78 per cent. of the organic aluminium compound had suffered decomposition. In another experiment a similar residue was gradually heated to 145°, when the frothing became decided, and it was then analysed. 0·423 gram gave on solution in nitric acid and addition of silver nitrate 0·006 gram of silver iodide; and 0·576 gram gave on treatment with water and ignition 0·156 gram of alumina. These data, and considerations previously referred to, lead us to assign to the residue at this stage the percentage composition of—

1·23 aluminic iodo-propylate,
96·08 aluminic propylate,
2·69 alumina.

It was now heated *in vacuo*. A quantity of alcohol passed over, followed by 1·8 gram of a dense liquid, which solidified on cooling.

This small yield of what presumably was aluminic propylate led us to think that the large amount of decomposition which must have taken place was occasioned by the alcohol containing water. A portion of it was therefore digested with anhydrous potassic carbonate, then with caustic baryta, which treatment increased the boiling point about a degree. An experiment made with it similar to the last gave, however, but a slight increase in the quantity of the aluminium distillate, viz., 2 grams. But in another trial, where the whole distillation was done *in vacuo*, 4·6 grams of the aluminium compound passed into the first receiver, which shows that the decomposition is mainly due to temperature.

Aluminium was estimated in each of the distillates, with the following results, stated in 100 parts:—

I.	II.	III.	$Al_2(C_3H_7O)_6$.
12·73	14·25	13·0	13·44

which numbers agree as well as could be expected, considering the nature and mode of preparation of the substance analysed, with those calculable on the supposition that the compound obtained as described is the third member of the series of aluminic alcohols, viz., aluminic propylate, $Al_2(C_3H_7O)_6$.

Isopropyl Alcohol.

In our paper on the action of the couple upon the two propyl iodides (*Chem. Soc. J.*, 1873, **26**, 961), it was pointed out that the iso-iodide was the more readily decomposed; and, further, that zinc iso-propide, which we obtained in small quantity, splits up at a temperature of 132° into zinc and hydrocarbon gases, whilst the normal zinc compound distils without material change at 146°. We have just shown that the normal alcohol decomposes readily in presence of aluminium and its iodide, and the fact of the greater instability of the two derivatives of the iso-alcohol led us to expect that it would undergo decomposition still more rapidly in presence of aluminium and aluminic iodide. On heating the reagent, however, with a specimen of the alcohol that distilled between 82° and 85°, not a trace of decomposition was observable, which unexpected result induced doubts as to whether the substance employed was really isopropyl alcohol. To place this matter beyond dispute, a portion of the specimen was boiled with strong aqueous hydriodic acid, when an oily compound was produced, having the boiling point and specific gravity of isopropyl iodide. This iodide, when heated to 50° with the copper-zinc couple, underwent decomposition in a manner which left no doubt regarding its being the iodide of isopropyl alcohol.

Aluminic Isobutylate.

Isobutyl alcohol boils, according to Linnemann, at 108·4°, and according to Chapman and Smith at 109°. The alcohol we have employed boiled at 108—109°. In an experiment where 4 grams of aluminium, 2 grams of iodine, and 40 c.c. of the alcohol were heated to 100°, the first litre of hydrogen was evolved in 7 minutes, the second litre in 4 minutes, the third in $3\frac{1}{2}$, and the fourth in $7\frac{1}{2}$ minutes. The action slowly continued for 15 minutes longer. The total gas collected measured 4,044 c.c. (corr.). The residue, after heating to 300°, was distilled *in vacuo*, when 16 grams of an aluminium compound free from iodide passed into the receivers. Portions of different specimens of this substance were analysed.

I. 0·478 gram dissolved in dilute nitric acid and aluminium precipitated by ammonia, gave 0·0982 Al_2O_3.

II. 0·689 gram, treated with water, dried at 100°, and ignited, gave 0·1473 Al_2O_3.

III. 0·2005 gram, treated as in II, gave 0·0425 Al_2O_3.

IV. 0·2457 gram, burnt with oxygen and oxide of copper, gave 0·5255 CO_2 and 0·226 H_2O.

These results, when set out as under—

		Calculated.	Found. I.	II.	III.	IV.
Al_2	55	11·15	10·97	11·41	11·31	—
C_{24}	288	58·43	—	—	—	58·32
H_{54}	54	10·95	—	—	—	10·22
O_6	96	19·47	—	—	—	—
$Al_2(C_4H_9O)_6$	493	100·00				

show that the body examined agrees in composition with the formula $Al_2(C_4H_9O)_6$, and, therefore, it being a derivative of the iso-alcohol, receives the name of aluminic isobutylate.

Aluminic Amylate.

The amylic alcohol of fermentation boils, according to various authorities, from 128—132°. That which we have employed boiled at 129—131°.

In illustration of the behaviour of aluminium and aluminic iodide with this alcohol, we subjoin the details of an experiment. 4 grams of the metal, 2 grams of iodine, and 40 c.c. of the alcohol were heated at 100°. The first litre of gas collected in four minutes, the second in two minutes, the third in two minutes, and the fourth in five minutes, showing that the action is decidedly more rapid with this than with the other alcohols. The total hydrogen obtained measured 3,985 c.c. (corr.). The residue heated to 300°, and *in vacuo*, gave 14 grams of an aluminium distillate, which, as well as another specimen prepared in like manner, were analysed.

I. 1·79 gram, dissolved, &c., gave 0·3056 Al_2O_3.
II. 0·6235 gram, treated with water, &c., gave 0·112 Al_2O_3.
III. 0·2815 gram, burnt with oxygen and copper oxide, gave 0·6455 CO_2 and 0·293 H_2O.

		Calculated.	Found. 1.	II.
Al_2	55	9·53	9·12	9·59
C_{30}	360	62·39	—	62 53
H_{66}	66	11·44	—	11·56
O_6	96	16·64	—	—
$Al_2(C_5H_{11}O)_6$	577	100·00		

The analytical numbers, as shown by the above statement of results, agree with the formula $Al_2(C_5H_{11}O)_6$, which is that of the fifth member of the series of aluminic alcohols, viz., aluminic amylate.

Cetyl Alcohol.

Methyl alcohol, as has been shown, does not undergo decomposition when boiled with aluminic iodide and aluminium, but this may arise from the low boiling point of the liquid. The difference in the rate at which the other alcohols part with hydrogen under analogous conditions is not well marked. The study of the action of the reagent upon a much higher member of the series it was thought would show definitely whether the stability of these compounds, which may be presumed to be of the same constitution, increases or not with their molecular weight, and also whether the replacement of hydrogen might be expected to take place in the intermediate members not examined.

Cetyl alcohol, $C_{16}H_{33}OH$, being the first solid member of the series, and sufficiently removed from amylic, was selected. This compound, gradually heated with Al_2I_6, underwent no visible change until between 200° and 250°, when action was indicated by the solidification of the melted contents of the flask. On treating this solid product with alcohol, aluminic hydrate was found in the residue, and cetyl alcohol and a solid organic iodide—presumably cetyl iodide—in solution. The action, therefore, appears to be one of double decomposition, and to accord with the equation—

$$6C_{16}H_{33}OH + Al_2I_6 = 6C_{16}H_{33}I + Al_2(HO)_6.$$

The alcohol gradually heated with Al_2I_6 and aluminium gave a little hydrogen; but at about 200° the gas evolution ceased, 100 c.c. having been collected. The contents of the flask were solid, and resembled the product of the action of heat on the alcohol and Al_2I_6 alone. On heating with free iodine and aluminium, about 150 c.c. of hydrogen were evolved as the temperature rose to 150°, when the evolution of gas quickly ceased as before, the contents of the flask having solidified.

In each of the experiments, 18·5 grams of the alcohol (about 10 c.c. when melted) were employed. In the first also 2 grams of Al_2I_6; in the second, 2 grams of Al_2I_6 and 0·5 gram of aluminium; and in the third, 2 grams of iodine and 0·5 gram of aluminium.

We conclude that cetyl alcohol is much more stable in presence of Al_2I_6 and aluminium than amylic alcohol, or the other members of the series which have yielded to these reagents, and that under their influence hydrogen is evolved and aluminic cetylate accordingly formed, but that the temperature at which this action takes place, being so close to that at which the double decomposition occurs previously referred to, prevents any quantity of this compound being produced.

Monohydric Alcohols of other Series.

Allyl alcohol.—After a preliminary trial or two, which showed that aluminic iodide could be boiled with this compound without either substance undergoing change, 2·2 grams of the iodide were dissolved in 20 c.c. of the alcohol, and heated with 1 gram of aluminium in the usual manner. Gas was slowly evolved for about an hour, when it almost ceased, 550 c.c. having been collected. The gas burned with a luminous smoky flame, and contained 37 per cent. by volume of an olefine, the remainder being hydrogen.

Another experiment was made by heating 20 c.c. of alcohol with 2 grams of iodine and 1 gram of aluminium. In 15 minutes 700 c.c. of gas were evolved, and in 10 more minutes action ceased. The whole of the aluminium was used up, and the gas collected measured 870 c.c., of which 270 c.c. were absorbed by bromine, the remainder being hydrogen. The compound produced by the union of a part of the gas with bromine, possessed the properties of propylene dibromide, showing that the hydrocarbon gas was propylene.

The explanation of these results is probably as follows:—The initial action is doubtless identical in character with that which takes place with the alcohols of the methyl series. In place, however, of the whole of the freed hydrogen escaping, as in the action with these compounds, about 30 per cent. of the gas, after decomposing the alcohol, enters into combination with both its negative and positive radicals, forming propylene and water, thus:—

$$C_3H_5OH + H_2 = C_3H_6 + H_2O.$$

Aluminic allylate, some of which must have been formed, could not be isolated by the distillation *in vacuo* of the non-gaseous products of this reaction. Little, however, of this compound may have existed at any moment, for as soon as any appreciable quantity of water had been formed by the hydrogenisation of the hydroxyl group of the alcohol, the reagents may have acted upon the water then present in preference to the alcohol.

Phenyl, Cresyl, and Thymol Alcohols.—Aluminium in presence of aluminium iodide, very rapidly decomposes these compounds at 100°, hydrogen being evolved equivalent to the metal employed, and aluminic phenylate, cresylate, or thymolate formed. The aluminium compounds cannot be obtained in a pure state by distillation *in vacuo*, but on heating the respective alcohols to about 200°, with the theoretical amount of aluminium, and enough iodine to start the action, and pouring off the semi-fluid product, they were obtained approximately pure. Thus a specimen of the phenylate prepared as described gave on analysis 9·49 per cent. of aluminium, the calculated being 8·97; a

specimen of cresylate 7·57, the calculated being 7·89; and a specimen of thymolate 5·96, the calculated being 5·79.

The phenylate hardens as it cools, whilst the cresylate and thymolate remain plastic for some considerable time.

Aluminium itself when boiled with phenyl and cresyl alcohols, very slowly decomposes them, phenyl alcohol being the more readily acted upon. Thymol does not appear to act at all on the metal, when boiled with it.

Benzyl Alcohol.—The hydrogen in this alcohol is also replaced by aluminium in presence of aluminium iodide. The action is very violent, the greater part of it being over in a few seconds. The aluminium compound undergoes complete decomposition on heating *in vacuo*.

Aluminium alone has no action on this compound, but aluminic iodide readily decomposes it on gently heating, an organic iodide having a violent action on the eyes and skin—probably benzylic iodide —being produced.

Naphthol.—At a temperature between its melting and boiling points, this alcohol is acted on by aluminium alone, hydrogen being evolved equivalent to the metal. The aluminic naphtholate, as in the case of the phenol compounds, does not distil *in vacuo*. The naphthol used was the β-naphthol, melting at 121—122° C.

Alcohols of other Atomicities.

Ethylene Alcohol.—When a solution of aluminic iodide in this alcohol was heated to a little above 100°, the mixture turned brown, and at about 160° a few bubbles of gas were produced containing an olefine. When heated to a higher temperature, a liquid having a lower boiling point than the alcohol was formed, which, from its action upon potassium and anhydrous copper sulphate, was concluded to be water. When heated with Al_2I_6 and aluminium or aluminium and free iodine, little or no difference was noticed in the action until the liquid referred to, collecting in the tubule of the condenser, fell into the flask, when after each drop a few bubbles of gas escaped, probably hydrogen, from its decomposition. We conclude, therefore, that the basic hydrogen of this alcohol is not replaced by the reagents employed.

Propenyl Alcohol (*Glycerol*).—Aluminic iodide dissolves somewhat slowly in this compound, but when the mixture is heated to about 140°, both substances undergo decomposition, aluminic hydrate, free iodine, and an oily body having the properties of allyl iodide being produced. The reaction doubtless accords with the equation :—

$$2C_3H_5(HO)_3 + Al_2I_6 = Al_2(HO)_6 + 2C_3H_6I + I_4,$$

from which it would follow that were the substances heated in presence of metallic aluminium, the sole products of the chemical change would be aluminic hydrate and allyl iodide. The experiment, details of which follow, show that this is the case :—

4 grams of aluminium iodide, and 2 grams of aluminium foil were heated with 30 c.c. of dry glycerine* until the reaction was completed.

Hydrogen was not evolved nor any other gas. On further heating the product, 1·2 c.c. of the organic iodide distilled. The residue, being now almost solid, 30 c.c. of glycerol were added to it, and again heated, when 1·5 c.c. more of the iodide passed over, which together with the first portion, approximates very closely to the calculated amount.

Dr. Hodgkinson, working on the lines of our paper already referred to, has also obtained allyl iodide, and almost in amount corresponding to the iodide employed, by heating glycerol with aluminium and free iodine (*Chem. News*, 1877, p. 237).

General Properties.

The aluminic alcohols are non-crystalline, and solid at the ordinary temperature, and those obtained pure are yellowish-white in colour. They are all more or less decomposed on heating at the ordinary atmospheric pressure, but those of the methyl series distil at reduced pressures, affording the first examples of organic compounds containing both oxygen and a metal capable of distillation.† The solubility in alcohol, ether, and benzol, of those which have been obtained pure, are roughly indicated in the annexed table:—

Aluminic compound.	In alcohol.	In ether.	In benzol.
Ethylate.	Nearly insoluble.	Slightly.	Moderately.
Propylate.	Very slightly.	Slightly.	Moderately.
Butylate.	Moderately.	Very.	Very.
Amylate.	Moderately.	Moderately.	Very.

The aluminium-compounds of the methyl series possess in a marked degree the property of remaining fluid below their fusing points. Thus specimens of ethylate and butylate, which melted at 130° and 140° respectively, remained fluid at 70° for at least an hour; and a

* Obtained by bubbling hydrogen through the liquid heated to 160° for three days.

† In 1877 Conrad showed that another aluminic compound, $C_{18}H_{27}O_9Al$, and an analogous copper salt, are capable of distillation (*Liebig's Ann.*, **188**, 272).

specimen of amylate which melted at 70° remained fluid for days at the ordinary temperature. The propylate decomposes somewhere near its melting point, which was found to be about 60°. Another peculiarity of these bodies is that they solidify first into a transparent, or semi-transparent mass, but after the lapse of some days, they become opaque. The numbers given as the melting points we regard only as approximations, for different specimens of some of these compounds, especially the amylate, have been found to differ in this respect.

The specific gravities of the compounds at 4° C., were found to be, for the—

Ethylate, 1·147
Propylate, 1·026
Butylate, 0·9825
Amylate, 0·9804.

The action of water upon the ethylate was found to give aluminic hydrate and alcohol:—

$$Al_2(C_nH_{2n+1}O)_6 + 6H_2O = 6(C_nH_{2n+1}OH) + Al_2(OH)_6.$$

The ease with which the positive radical of the water, in this latter (probably typical) action, combines with the negative radical of the aluminic alcohols, points to a great number of probable syntheses; and from the atomicity and other chemical qualities of aluminium, it is very probable that compounds of very considerable interest will result therefrom.

Theoretical Note.

We have offered two possible explanations of the part which the relatively small quantity of aluminic iodide plays in these aluminium substitutions. The one for which we expressed a preference, as already mentioned, was the one requiring the formation of hydriodic acid in the first step of the reaction. No direct evidence, however, of the production of this substance was found until our experiments with the phenyl group of alcohols, when, on gently warming each of these compounds with aluminic iodide, an appreciable quantity of hydriodic acid was evolved. This matter is more fully discussed in our paper on the aluminium-iodine reaction in the *Proceedings of the Royal Society*.

II.—*Synthetical Production of New Acids of the Pyruvic Series.* (Continued.)

By Edward Moritz.

Part II. *Isobutyryl- and Butyryl-formic Acids.*

In accordance with my intentions, I have applied the reactions which I used for the preparation of propionylformic acid to the formation of higher acids of the same series.

I first experimented on isobutyryl compounds. Before starting the regular work I endeavoured to hit upon a better method for preparing the cyanide, and in doing so I obtained a very fair yield by heating 50 grams of silver cyanide with 40 grams of isobutyryl chloride on an oil-bath for about three-quarters of an hour, and as this lightened the work considerably, I preferred to use this modification of the method to the old one. However, when I had used up all my substance (about 400 grams), I found, on fractioning the crude product, that I only obtained just about as much cyanide as the preliminary experiment yielded, for which I had only used about 40 grams. Naturally there was none to spare for an analysis, so I converted the 6 grams of cyanide into the amide. The cyanide boils at 117—120°.

Isobutyrylformic Amide.—The amide was prepared exactly in the same way as has already been described. From the 6 grams of isobutyryl cyanide I obtained about $\frac{2}{10}$ gram of amide. It fuses at 125—126°. One analysis made unfortunately came to grief.

Di-isobutyryl Dicyanide.—In the preparation of the cyanide there was a vast quantity of substance which boiled above 160°. This was carefully fractioned, and about 70 grams of nearly pure substance obtained. A small portion for analysis was then purified by repeated fractional distillation. It boils at 226—228°. The following were the results obtained by analysis:—

(1.) 0·195 gram substance gave 0·4442 gram CO_2 and 0·1309 gram H_2O.

(2.) 0·2223 gram substance gave 0·5055 gram CO_2 and 0·1487 gram H_2O.

Nitrogen determination 0·2091 gram substance gave 0·209 gram Pt.

	Theory.		Found.	
C_5	60	61·85	(I) 62·12	62·01
H_7	7	7·21	7·45	7·42
N	14	14·43	14·13	—
O	16	16·51	—	—
	97	100·00		

The vapour-density determined according to Hofmann's method gave results which leave no doubt as to its being a di-cyanide. The specific gravity of the liquid is 0·96. It does not solidify at −15°. It is intensely poisonous—traces of its vapour produce giddiness, headache, and nausea; large quantities, illness for several days.

On being saponified with the theoretical quantity of hydrochloric acid (sp. gr. 1·22) in closed tubes it gave the amide of isobutyrylformic acid, agreeing approximately in melting point to the amide obtained from the monocyanide. The difference is caused by traces of polymeric cyanide, from which it cannot be purified by fractional sublimation, or by solution and crystallisation from ether. This admixture naturally lowers the melting point and increases the percentage of nitrogen, so that an analysis of the amide for nitrogen came about 5—10 per cent. too high.

0·1734 gram substance gives 0·1562 gram Pt.

	Theory.		Found.
C_5 ..... H_9 ..... O_2	101	87·83	—
N	14	12·17	12·77
	115	100	

Acid.—The acid was prepared in the following way: —7½ grams of the polymeric cyanide and 10 grams of hydrochloric acid (sp. gr. 1·22) were brought into a small stoppered bottle and left for two days. The mixture was then brought into a flask, to which was now added 14 grams of hydrochloric acid (sp. gr. 1·1). The fluid was not homogeneous. There were two distinct layers, which did not mix with one another. Three or four other portions were treated in a similar way, and when all were prepared up to this point the whole was divided into two portions, and each was boiled separately on the water-bath for about an hour, after which each part was shaken up with ether. The ethereal solution, after separation from the aqueous part by mechanical means, was dried over calcium chloride, the ether driven off, and the residue fractioned *in vacuo*.

Isobutyric acid boils at 68° at a pressure of 45 mm. After the isobutyric acid had come over, that portion was retained as the ketonic acid which boiled at 85—95° at the above-mentioned pressure. The thermometer was constant at 92—93°; 18 grams of liquid were obtained between these degrees. The product smelt strongly of isobutyric acid, although a burnt smell (characteristic of ketone acid) was also perceptible. It was, as will be seen by the analysis, a mixture of isobutyric and isobutyrylformic acids.

The following are the analytical results:—

(1.) 0·2829 gram substance gave 0·2215 gram H_2O and 0·558 gram CO_2.

(2.) 0·2205 gram substance gave 0·1722 gram H_2O and 0·4328 gram CO_2.

A third analysis was made by Dr. Claisen, of which I append results:—

Ketonic acid.	Theory.		Found.		
			(1.)	(2.)	(3.)
C_5	60	51·72	53·79	53·52	53·53
H_8	8	6·9	8·69	8·68	8·60
O_3	48	41·38	—	—	—
	116	100			

Theory.		Isobutyric acid.
54·54	48	C_4
9·09	8	H_8
36·37	32	O_2.

These results agree so closely that they leave little doubt as to the mixture of the acids.

A silver salt was prepared (indirectly from the calcium salt) which points to the same percentage composition of the mixture: 0·2364 gram substance gave on ignition 0·1298 gram Ag.

Ketonic acid salt.	Theory.		Found.	Theory.		Isobutyric acid salt.
C_5 H_7 O_3	115	51·57	—	44·62	87	C_4 H_7 O_2
Ag	108	48·43	54·90	55·38	108	Ag
	223	100		100	195	

Nothing more could be done with the acid; its salts could not be separated from the corresponding salts of the fatty acid series, nor could the acids be separated by fractional distillation.

Two interesting bodies were obtained from the di-isobutyryl dicyanide in the following way:—If, in the preparation of the acid (from the polymeric cyanide) after the addition of the dilute hydrochloric acid, the mixture be not boiled, but poured into cold water, oily drops form at the bottom which presently solidify. These oily drops cannot consist either of di-isobutyryl dicyanide or of isobutyric acid, as both are lighter than water. If, after complete solidification (which generally takes about two hours), the solid be filtered off and

afterwards dried, it will be found on further investigation that this white amorphous substance can be separated into two substances, both white and amorphous. Both are nitrogenous, but they are loth to give up their nitrogen; no trace of ammonia can be perceived till they have been heated for some time in the solid state with dry soda-lime. They can be separated by their difference in solubility in sodium carbonate. The soluble one fuses at 187—188°, the insoluble one at 207—208°; it is soluble, however, in sodium hydrate, but is reprecipitated from its solution by carbonic acid. I could not investigate these substances any further as I had not sufficient of them, nor had I sufficient polymeric cyanide left to prepare any more. They are both very light and voluminous substances, and thus deceive one at first as to the quantity obtained.

I now close this chapter and pass on to the normal butyryl compounds.

This time I had recourse again to Huebner's preparation of the cyanide from the chloride. 750 grams of butyryl chloride were altogether used, portions of 16 grams being heated up in closed tubes with 20 grams of silver cyanide. It was found best to first fill into the tube seven-eighths of the silver cyanide, then to pour in the liquid by means of a thistle-funnel, and then to add the remaining silver cyanide, after which the tube was immediately sealed. This arrangement causes the liquid and solid to come more into contact with each other than any other. After all the tubes had been heated up for the required time they were opened and the contents brought into six small flasks, which all fitted on to the same distilling apparatus. Each flask was then heated in turn on the sand-bath over a 15-flame Bunsen burner, finishing with the free flame of an ordinary burner. The crude product so obtained was distilled up to 110° with Linnemann's apparatus, so as to effectually get rid of all prussic acid and undecomposed butyryl chloride; after this an ordinary **T**-tube was substituted, and the rest fractioned in the ordinary way. The crude product repeatedly fractioned gave about 40 grams of cyanide, boiling between 133—140°. When perfectly pure it boils at 133—137°. I considered it unnecessary to analyse the cyanide.

Butyrylformic Amide.—6 grams of the cyanide were saponified in the usual way for the preparation of the amide, of which $\frac{8}{10}$ gram were obtained pure. It melts at 105—106°.

The following are the analytical results:—

0·1621 gram substance gave 0·3084 gram CO_2 and 0·1185 gram H_2O.

Nitrogen estimation 0·188 gram substance gave 0·157 gram Pt.

	Theory.		Found.
C_5	60	52·17	51·88
H_9	9	7·77	8·12
N	14	12·17	11·84
O_3	32	27·89	—
	115	100	

Di-butyryl Di-cyanide.—The residue in the preparation of the cyanide was fractioned again, but instead of, as usual, getting a stable polymeric cyanide, I only obtained 10 grams out of an exceptionally large quantity of residue. This is due to its unstability; even below its boiling point it splits up into a number of decomposition products, among others the monocyanide. When pure it boils at 232—235°.

The following are the analytical results:—

0·1855 gram substance gave 0·1328 gram H_2O and 0·422 gram CO_2.

0·1835 gram substance gave 0·1825 gram Pt—nitrogen determination.

	Theory.		Found.
C_5	60	61·85	61·88
H_7	7	7·46	8·12
N	14	14·43	11·84
O	16	16·26	—
	97	100	

It will be noticed that in the last analyses the water comes exceptionally high; this was due to the extreme heat of the weather and to the fact that closed tubes were always used.

Butyrylformic Acid.—36 grams of cyanide were used for the preparation of the acid and were divided into six portions. 6 grams of the cyanide and 2 grams of hydrochloric acid (sp. gr. 1·22) were brought together in a small flask provided with a well-fitting cork and left to stand in iced water for some hours. When the mass had become apparently solid 2 grams more of the same hydrochloric acid were added. All the rest was treated in the same way, and then 11 grams of hydrochloric acid of sp. gr. 1·1 were added to each portion. The whole contents of the six flasks were now divided into two portions and a little water added to each. Instead of boiling, as had always been done before, the acid was extracted at once with ether, the ethereal solution separated, dried over chloride of calcium, and the ether distilled off. The residue was now fractioned *in vacuo*. Pure butyric acid boils at 100° at a pressure of 82—84 mm.; about 15° higher the ketonic acid comes over. It has a characteristic burnt

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smell, but after standing for some days it gradually evolves a smell of butyric acid; in fact, it can be seen by the analyses that follow that it gradually becomes impure; nevertheless it is moderately stable, it can be distilled at the ordinary pressure, with only partial decomposition; it then boils at 180—185°. It was not pure enough to give by reduction normal α-oxyvaleric acid.

The following are the analytical results, the fifth combustion being done by an assistant according to Kopper's method, which gives the water more correctly than other methods:—

(1.) 0·2199 gram substance gave 0·4179 gram CO_2 and 0·149 gram H_2O.

(2.) 0·1744 gram substance gave 0·335 gram CO_2 and 0·1283 gram H_2O.

(3.) 0·2919 gram substance gave 0·576 gram CO_2 and 0·2144 gram H_2O.

(4.) 0·175 gram substance gave 0·3346 gram CO_2 and 0·1275 gram H_2O.

The fourth analysis was, with the substance, distilled at the ordinary pressure.

Ketonic acid.	Theory.		Found.				
			(1.)	(2.)	(3.)	(4.)	(5.)
C_5....	60	51·72	51·83	52·3	53·81	52·14	52·55
H_8....	8	6·9	7·53	8·17	8·16	8·08	7·3
O_3....	48	41·38	—	—	—	—	—
	116	100					

Theory.		
54·54	48	C_4
9·09	8	H_8
36·37	32	O_2
100	88	

This finishes my results on these ketonic acids. Certainly the higher the number in the series the more difficulty experienced in the preparation of the corresponding cyanide, amide, and acid. What is essentially necessary to the success of further investigations on the subject is an improved method for the preparation of the cyanides of the acid radicles.

I may mention that some months ago a method of preparing the cyanides of substituted acid-radicle (trichloracetyl cyanide) was found, which gives 75 per cent. of the theoretic. It consists in heating in an apparatus provided with an inverted condenser a

mixture of the bromide of the substituted acid radicle with the corresponding amount of mercuric cyanide and then distilling off. I tried similar experiments with the acid-radicle bromides themselves, but obtained only negative results.

III.—*The Ancient Alum Well at Harrogate.*

By R. Hayton Davis, F.C.S.

Dr. Thomas Garnett, a physician in practice at Harrogate in the year 1791, and afterwards Professor of Chemistry at the Royal Institution, London, in his treatise on "The Mineral Waters of Harrogate," wrote as follows:—

"In one of the sulphur wells situated in the bog, I have discovered alum, and I suspect salited clay. In a chalybeate water near the road, and not far from the Crescent garden, the iron is dissolved by the muriatic acid."

Dr. Adam Hunter, a physician resident in Leeds, in his book entitled "The Waters of Harrogate and its Vicinity," published in 1830, commenting upon these statements, says:—

"The reader will, I believe, look in vain for alum or muriate of iron in the waters referred to."

The discovery of ferrous chloride in 1865 in one of the Harrogate Spas, near the site indicated by Dr. Garnett, and the substance of my paper this evening, strongly support Dr. Garnett's observations. So far back as 1733 Dr. Thomas Short, of Sheffield, F.R.S., mentions an alum well in the bog-field at Harrogate, describing its position, the nature of the ground, and the experiments he made with the water.

Dr. Garnett, referring to these observations, says:—

"From Dr. Short's experiments it seems to have been a chalybeate water in which the iron is held in solution by the sulphuric acid;" then he adds: "I have found two or three springs of this kind in the bog, very near some sulphur wells."

Since Dr. Garnett's residence in Harrogate a period of 80 years elapsed, and the existence of the alum well passed quite out of memory. It was not until 1870, when excavations were made in the bog-field for the purpose of increasing the supply of sulphur-water, that this aluminous water again came to light; the excavation was afterwards deepened, earthenware pipes were put down, forming a well about 4 feet deep and 14 inches diameter, where the water slowly collects.

This aluminous water is of a pale reddish-brown colour, strongly acid to litmus and very astringent taste; after keeping a short time, if exposed to the air, a portion of the iron is precipitated as basic sulphate, and the protosulphate gradually changes into the ferric salt.

The ground in its vicinity is strongly acid to litmus, tastes austere, even after heavy and continuous rains; depressions in the ground after a shower, more particularly in summer, are found filled with water corresponding in colour and taste with that in the well.

Immediately under the peaty soil in various places around the well there is a layer of deposit having a sulphur-yellow colour; its appearance has no doubt given rise to the statements of Dr. Short and other old writers, respecting the prodigious quantities of sulphur to be found in the locality. I find, on examination, it contains about 60 per cent. soluble in hydrochloric acid, consisting of SO_3 14·60, Fe_2O_3 29·32, and small quantities of Ca, Mg, Na, &c.; it bears a remarkable resemblance to two of the ferruginous deposits found in the neighbourhood of the Caspian Sea, the analyses of which by A. Frenzel are published in the September number of the Journal of this Society.

To revert to the alum well: its position is remarkable, in being almost surrounded by sulphur wells, which circumstance, together with the surface of the soil being so strongly impregnated with the constituents of the water, strengthens the opinion that the water is of comparatively superficial origin, and is continually produced by natural causes.

The old deposits from the chalybeate waters situate on higher ground, and the sulphur waters rising through the stratum of shale at a lower level, appear to be the factors in the production of this remarkable water.

The Ancient Alum Well at Harrogate. The Quantities are in Grains per Gallon. Sp. gr. 1005·43.

Fe.....	47·59	Ferric sulphate.....	78·76
Al.....	14·24	Ferrous sulphate	69·33
Ca	16·74	Aluminium sulphate	89·47
Mg	11·47	Calcium „	56·91
K.....	1·40	Magnesium „	57·38
Na	13·36	Potassium „	3·14
NH_4.....	0·59	Ammonium „	2·19
SO_4	265·44	Sodium chloride	33·96
Cl.....	20·60	Silica.....	3·27
SiO	3·27		
	394·70		394·41

Total residue dried 360—380° 397·25

IV.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. VII. *On Bismuth and Bismuth Compounds.*

By M. M. Pattison Muir, M.A., F.R.S.E., Caius Prælector in Chemistry; G. Bernard Hoffmeister, B.A., B.Sc.; and C. E. Robbs; Scholars of Caius College, Cambridge.

Part I.—*On the Oxides and Hydrates of Bismuth.*

A series of papers has been published in this Journal by one of us, on various compounds of bismuth. It is proposed now to study in more detail the chemical habitudes of groups of these compounds.

§. *Preparation of Oxides and Hydrated Oxides of Bismuth.*

A large amount of work on the oxides of bismuth has been published; methods for preparing these salts are not yet, however, clearly established.

Observers are all agreed as to the preparation of bismuthous oxide: this forms the starting point in the preparation of the other oxides.

1. Our experiments have convinced us that by boiling previously prepared bismuthous oxide with potash and alkaline hypochlorite, it is very difficult, if not impossible, to obtain a pure oxide higher than bismuthous oxide (see Arppe, *Pogg. Ann.*, **64**, 237; and Schrader, *Annalen*, **121**, 204). A brown substance is certainly produced, but analyses show that the composition is not homogeneous: in one instance we found 91·5, in another 94·5 per cent. of bismuth. This brown substance does not lose weight until heated to 250°; it does not, therefore, contain bismuthic oxide. It dissolves slowly in strong nitric acid with evolution of oxygen; it therefore contains an oxide higher than bismuthous oxide.

We obtained from Messrs. Hopkin and Williams a black-brown powder labelled "peroxide of bismuth," which, as Messrs. Hopkin and Williams kindly informed us, was prepared "by boiling oxide of bismuth with hypochlorite of soda containing a considerable excess of caustic soda." This substance contained 85·67 per cent. of bismuth (mean of 85·5 and 85·85), 0·76 per cent. moisture, and 1·5 per cent. sodium. The percentage of bismuth calculated on the dry salt free from soda amounted to 88·10 (Bi_2O_4 requires 86·78, and Bi_2O_3 89·75 per cent.). This salt when boiled for some hours with very dilute nitric acid became brown, and was then free from soda. Dried at

130°, it now contained 82·46 per cent. bismuth (mean of 82·57 and 82·35), and 0·30 per cent. moisture. The original black "peroxide" began to change colour and lose weight at 250—260°. It dissolved in hydrochloric acid with evolution of chlorine, and in hot nitric acid with evolution of oxygen. Its specific gravity was 6·77. We therefore conclude that this substance, although containing much hypobismuthic oxide, was not a pure salt.

2. In a paper by one of us, the preparation of hypobismuthic oxide has been described (this Journal, 1877, i, 28); we have somewhat modified that method, and have obtained good results. Bismuthous oxide is suspended in a large excess of potash solution of about 1·35 sp. gr.; the potash is kept nearly boiling, and chlorine is passed in until the precipitate is homogeneous, and of a dark chocolate-red colour; the precipitate is washed free from potash with hot water, kept in contact with dilute nitric acid (about 1 acid to 20 water) for 12 or 16 hours, until the colour of the solid has changed to brownish-yellow, washed free from acid, boiled for about an hour with a strong solution of sodium, or calcium, hypochlorite (preferably the former), till a perfectly homogeneous, yellow-brown, heavy powder is produced, which settles readily. This is washed with hot water till free from chlorine and alkali, and dried at 180—200° for two or three hours. A specimen thus prepared contained 86·81 per cent. of bismuth (mean of 86·54 and 87·08), and lost 3·17 per cent. when converted into bismuthous oxide by heating.

Bi_2O_4 requires 86·78 per cent. bismuth, and loses 3·30 per cent. on heating.

The prolonged digestion with nitric acid serves to dissolve any bismuthous oxide which may have escaped oxidation, and also to deoxidise the bismuthic oxide which has been formed; subsequent treatment with alkaline hypochlorite appears to convert any traces of bismuthous oxide yet present into hypobismuthic oxide.

3. The following method of procedure yields pure bismuthic oxide:—Bismuthous oxide is suspended in a large excess of very concentrated potash solution; specific gravity 1·37 to 1·38. The liquid is kept nearly boiling, and chlorine is passed in until the precipitate is quite homogeneous, and of a dark-red colour; the precipitate is then washed with hot water, until free from potash, and then with cold water, until every trace of chloride is removed; if any chloride is allowed to remain it is decomposed by the nitric acid subsequently added with formation of hydrochloric acid, which acts on the bismuthic oxide; it is then boiled for a very few minutes with concentrated nitric acid (whereby any remaining bismuthous or hypobismuthic oxide is removed) until all is distinctly scarlet, washed repeatedly and quickly with boiling dilute nitric acid, each quantity of acid being more dilute

than the preceding, and finally the acid is completely removed by washing with cold water; the scarlet precipitate is then dried at 125° for three or four hours.

A specimen thus prepared contained 83·87 per cent. bismuth (Bi_2O_5 requires 84·0 per cent.). Heintz (*Pogg. Ann.*, **63**, 559) recommends a method of preparation very similar to the above. Arppe states that anhydrous bismuthic oxide is obtained by the action of chlorine on bismuthous oxide suspended in *moderate excess* of strong potash solution. We have, however, failed (as Schrader did) to obtain the oxide by this process, the product being always a hydrated oxide, or mixture of hydrated oxides. Arppe does not state the temperature or conditions under which the salt which he obtained was dried.

We have attempted, but without success, to prepare oxides intermediate between bismuthic and hypobismuthic oxide (see Arppe, *loc. cit.*).

4. No hydrates of hypobismuthous oxide are known with certainty. Facts will be mentioned in the sequel which seem best explained by supposing that hydrates of this oxide are really formed during the oxidation of the oxide in presence of water.

About 0·5 gram of moist hypobismuthic oxide, prepared as described in par. 2, was placed over sulphuric acid for 12 hours; it then lost 6·5 per cent. on heating to 190—200°; a portion of the same substance dried at 100°, lost 6·9 per cent. at 200°. The salt contained 81·16 per cent. bismuth. $Bi_2O_4.2H_2O$ requires 80·77 per cent. bismuth, and 6·92 per cent. water.

Thus the dihydrate, $Bi_2O_4.2H_2O$, is produced by drying the product of the oxidation of bismuthous oxide under the conditions stated in par. 2 over sulphuric acid, or at 100°. A similar result was obtained by Schrader, (*loc. cit.*).

Another specimen, after drying at 110°, lost 4·5 per cent. at 200°, which is rather more than the loss required by the monohydrate, $Bi_2O_4.H_2O$, viz., 3·59 per cent.

One of us has described the monohydrate, $Bi_2O_4.H_2O$, prepared by the action of chlorine in presence of aqueous potash on bismuthous oxide (this Journal, 1877, i, 28). The greater part of the hydrated oxide now prepared was a product of the deoxidation of $Bi_2O_5.xH_2O$. It would appear that hypobismuthic dihydrate is produced by the deoxidation of hydrates of bismuthic oxide in presence of water, and hypobismuthic monohydrate by the oxidation of bismuthous oxide in presence of water, and under special conditions of concentration of potash, amount of chlorine used, &c.; probably, if the hydrate $Bi_2O_3.H_2O$ be formed at an early stage of the process, the oxidised product is $Bi_2O_4.H_2O$; if $Bi_2O_3.2H_2O$ be produced, oxidation results in the formation of $Bi_2O_4.4H_2O$ (see paragraphs 8 and 9).

About 0·25 gram of hypobismuthic oxide was exposed to the action of ordinary and of moist air, with the following results:—

Hypobismuthic Oxide.

In air.				Over water.			
Gained	0·92	p. c. in	70 hours	Gained	8·98	p. c. in	70 hours
,,	1·50	,,	140 ,,	,,	9·58	,,	140 ,,
,,	2·19	,,	210 ,,	,,	10·23	,,	210 ,,
,,	2·81	,,	280 ,,	,,	10·23	,,	280 ,,

Bi_2O_4 to $Bi_2O_4.H_2O$ requires 3·72 per cent. Bi_2O_4 to $Bi_2O_4.2H_2O$ requires 7·44 per cent. Bi_2O_4 to $Bi_2O_4.3H_2O$ requires 11·16 per cent.

In ordinary air the monohydrate is therefore slowly produced; but in moist air the oxide quickly passes into the dihydrate, and goes towards the trihydrate, but before this is completely reached deoxidation begins (see paragraphs 8 and 9).

5. The following results show the rate of hydration of bismuthous oxide; about 0·35 gram was used.

Bismuthous Oxide.

In air.				Over water.			
Gained	0·15	p. c. in	24 hours	Gained	1·83	p. c. in	24 hours
,,	0·30	,,	70 ,,	,,	1·83	,,	70 ,,
,,	0·30	,,	140 ,,	,,	1·98	,,	140 ,,

This oxide does not therefore take up a single molecule of water of hydration in moist air even after six days' exposure; in ordinary air only traces of water, probably hygroscopic, are assumed. The hydrates of this oxide are, it is well known, easily dehydrated; boiling with potash, or heating to a temperature below 100°, suffices to render these compounds anhydrous.

6. A quantity of moist bismuthic oxide, prepared as described in par. 3, after drying over sulphuric acid for seven days, lost 5·53 per cent. at 125°; after four days' further drying, it lost 3·47 per cent., and contained 80·81 per cent. bismuth. $Bi_2O_5.H_2O$ requires 81·08 per cent. bismuth, and 3·47 per cent. water. The salt was therefore bismuthic monohydrate.

The rate of hydration of bismuthic oxide is shown by the following numbers; about 0·5 gram was used:—

Bismuthic Oxide.

In air.				Over water.			
Gained	0·79	p. c. in	70 hours	Gained	3·36	p. c. in	70 hours
,,	1·09	,,	140 ,,	,,	3·92	,,	140 ,,
,,	1·42	,,	210 ,,	,,	4·48	,,	210 ,,

The monohydrate $Bi_2O_5.H_2O$, is therefore quickly produced in moist air, but the hydration scarcely proceeds further; in ordinary air, on the other hand, even after nine days, the oxide is only partially converted into the monohydrate. Bismuthic oxide, therefore, undergoes hydration rather less readily than hypobismuthic oxide; the hydration does not extend beyond a single molecule of water.

Bismuthic monohydrate also parts with its water of hydration at a lower temperature (125—130°) than that at which hypobismuthic dihydrate is rendered anhydrous (160°).

When bismuthic oxide is repeatedly moistened with water, and allowed to remain in the air, or when it is placed in contact with a large excess of water, it undergoes deoxidation, with production of a noticeable quantity of the white hydrate, $Bi_2O_3.2H_2O$, and also of a hydrate or hydrates of Bi_2O_4.

The brown oxide Bi_2O_4, after taking up rather more water than required to convert it into $Bi_2O_4.2H_2O$, began to appear whitish at the edges, and to lose weight slightly, showing that deoxidation was commencing.

Arppe (*loc. cit.*) states that bismuthic oxide does not take up water directly, but is converted into the monohydrate by the action of chlorine in presence of potash. Our experiments, we think, show that when exposed to moist air, this oxide does become hydrated; but inasmuch as the moist hydrate readily undergoes deoxidation, the best method of preparing the monohydrate is, undoubtedly, to proceed as described in par. 3, and to dry the product over sulphuric acid.

7. Boedeker (*Annalen*, **123**, 61) describes a brown salt, to which he gives the formula $Bi_2O_5.2H_2O$, prepared by the action of potassium cyanide on bismuth nitrate solution. We have prepared Boedeker's salt and analysed it, with results which agree fairly with the formula $Bi_2O_5.2H_2O$. The properties of this salt are, however, so peculiar, that a fuller account of it is reserved for a future communication.

§. *Properties of Oxides and Hydrates of Bismuth.*

8. When moist hypobismuthous oxide is exposed in air, it rapidly undergoes oxidation to the white hydrate $Bi_2O_3.2H_2O$; when the dry salt is moistened with water and exposed in air, oxidation proceeds much more slowly. We explain these facts by supposing that hydrates of hypobismuthous oxide are produced during the drying of the moist substance, and that in the oxidation of the dried oxide, in presence of water, formation of a hydrate of Bi_2O_2 precedes that of the hydrate $Bi_2O_3.2H_2O$.

An attempt to dry hypobismuthous oxide by heating in a current of carbonic anhydride did not give satisfactory results.

Hypobismuthous oxide, when kept in a stoppered bottle, very slowly passes into the white hydrate already mentioned. A quantity of the oxide so kept for three years had suffered oxidation to the extent of about 10 per cent.

The passage of Bi_2O_2 to $Bi_2O_3.2H_2O$ is attended with the evolution of a considerable quantity of heat; the oxidising substance is sensibly warm to the touch.

It has been already mentioned that bismuthic and hypobismuthic oxides, or the hydrates of these oxides, are partly deoxidised in presence of an excess of water, with production of $Bi_2O_3.2H_2O$. The deoxidation, especially of $Bi_2O_5.xH_2O$, is hastened by the action of direct sunlight. If a few drops of nitric acid be added to the water less deoxidation apparently occurs, but this seeming decrease is due to the solvent action exerted by the acid on the hydrates of bismuthous oxide which are produced.

9. The first product of the action of nitric acid on bismuthic oxide or hydrate is the hydrate $Bi_2O_4.2H_2O$ (Schrader): this has been fully confirmed. Thus a quantity of $Bi_2O_5.H_2O$ was boiled with 1 : 1 nitric acid until all was of an orange-red colour, the residue was washed and dried at 160°. The brown salt thus produced contained 87·11 per cent. of bismuth, and began to give off oxygen at 230°. Bi_2O_4 requires 86·78 per cent. bismuth. Very dilute nitric acid does not, however, bring about this change, unless the time of action be very prolonged. Two portions, about 5 grams each, of pure $Bi_2O_5.H_2O$ boiled with 100 c.c. water and 6 to 10 drops concentrated nitric acid, did not change colour, the residues when washed and dried over sulphuric acid, contained 81·47 and 82·2 per cent. bismuth, respectively, and 3·50 and 3·30 per cent. water. $Bi_2O_5.H_2O$ requires 81·08 per cent. bismuth and 3·47 per cent. water.

That dilute nitric acid exerts no oxidising action on hypobismuthic oxide is evident from the fact that portions of this oxide were not visibly changed when boiled with exceedingly dilute nitric acid, and that the residues, dried at 160°, contained 87·1 per cent. and 86·9 per cent. bismuth respectively. Bi_2O_4 requires 86·78 per cent. Somewhat more concentrated acid exerts a visible deoxidising action on Bi_2O_4: this oxide dissolves in concentrated nitric acid and more slowly in concentrated sulphuric acid, with evolution of oxygen, and in hydrochloric acid with evolution of chlorine.

Hypobismuthous oxide is rapidly oxidised to the white hydrate of bismuthous oxide by a few drops of nitric acid; addition of a little more acid dissolves the hydrate formed; if a moderate quantity of acid be added directly to the oxide, part of it goes into solution as nitrate, and metallic bismuth simultaneously separates; $3Bi_2O_2 + 12HNO_3 = 2Bi_2.6NO_3 + Bi_2 + 6H_2O$.

When hypobismuthous oxide was warmed with aqueous potassium permanganate, either alone or in presence of potash, the permanganate was reduced to manganate, and a dark brownish-red heavy substance was formed, which, after washing, dissolved slowly in concentrated nitric acid with evolution of oxygen, showing it to be Bi_2O_4, or, more probably, a mixture of this oxide and Bi_2O_5. Bismuthous oxide was not oxidised by boiling with aqueous permanganate; when potash was added and boiling was continued for some time, there was a very slight production of a higher oxide.

10. Arppe (*loc. cit.*) states that a red liquid, resembling dilute potassium permanganate solution and containing bismuth and potassium, is obtained by boiling bismuthic hydrate with potash.

Heintz (*Pogg. Ann.*, **63**, 559) says that Arppe conducted experiments in his presence, and that he obtained a liquid with a faint shade of green, and containing only traces of bismuth.

We have altogether failed to effect any change either in bismuthic or hypobismuthic hydrate by long-continued boiling with potash solution; the potash was all removable by washing with water.

In the preparation of these hydrates (by the action of chlorine on bismuthous oxide in potash) a red liquid is certainly produced, and if hydrochloric acid is added to this liquid, a reddish-white precipitate, containing bismuth and potassium, slowly separates. But we find that the colour of this liquid is due to small quantities of hydrates of the higher oxides suspended therein in an extremely finely divided state; if the red liquid be filtered through good paper, the filtrate is colourless, and contains neither bismuth nor potassium. We think that Arppe's so-called "potassium bismuthate" was a mixture of potash and hydrates of Bi_2O_4 and Bi_2O_5, obtained from this liquid.

11. Some details of the action of heat on various oxides of bismuth have been already given in previous papers. The following results concerning this action, and also the action of oxygen, hydrogen, and carbon monoxide, show the reciprocal stabilities of the oxides of this element:—

In each experiment about 0·5 gram of the oxide was placed in a test-tube, carrying a cork and two tubes, one to deliver, the other to carry off the gas; the test-tubes were heated in a water-, paraffin-, or air-bath; the temperatures are approximate only, and may be regarded as correct within 5°. The test-tube and its contents were weighed at the end of each period noted in the tables; the course of reduction was therefore discontinuous.

Oxygen was purified by passing through potash, and then through boiled sulphuric acid; hydrogen, by passing successively through pumice soaked in potash and in silver nitrate, and finally through boiled sulphuric acid; carbon monoxide was stored in a gas-holder, and passed

through potash and boiled sulphuric acid before use. The gases were passed at approximately the same rate in each experiment; no special device was however adopted.

The temperature of initial action of carbon monoxide was determined by the method described by Wright (this Journal, Trans., 1878, 1).

Heating in air was conducted with the same arrangement of tubes, but *no current* of air was passed over the heated oxides.

Hypobismuthous Oxide.

On account of the difficulty of obtaining this salt perfectly free from bismuthous oxide and hydrates, we have only a few results to offer.

It has been previously shown that this oxide, when heated in an open vessel in air, begins to absorb oxygen at 180° (this Journal, 1877, ii, 136); we find that oxidation begins in oxygen at about 140°, and is complete at 240°, after ten minutes' heating; that reduction begins, and is rapidly completed in hydrogen at 300—310°, and begins in carbon monoxide at about 250°.

Bismuthous Oxide.

I. Temperature of Initial Action of Carbon Monoxide (about 0·5 gram taken).

Temp.	Time in mins.	Turbidity in baryta-water.
100°	4	none
150	4	none
200	4	very faint

Reduction in carbon monoxide begins therefore at about 200°.

II. Reduction in Hydrogen (0·553 gram taken).

Temp.	Time in mins.	Loss in mgms.	Percentage loss.
245°	15	4	0·72
255	10	1	0·18
300	10	8	1·45

Total loss = 2·35 per cent. Bi_2O_3 to Bi_2O_2 loses 3·44 per cent.

Reduction to Bi_2O_2 is therefore not complete in hydrogen at 300° after 35 minutes' (discontinuous) action.

Appearance of residue at 300° was black-grey mixed with yellow specks.

Bismuthous oxide is not altered by heating in air or in oxygen.

Hypobismuthic Oxide.

III. Reduction in Carbon Monoxide (0·247 gram taken).

Temp.	Time in mins.	Turbidity in baryta-water.	Loss in mgrms.	Percentage loss.
80°	4	none	—	—
90	4	none	—	—
95	4	none	—	—
100	4	very faint	—	—
115	4	decided	—	—
115	10	—	3·0	1·21
125	10	—	0·3	0·12
155	10	—	1·2	0·50
175	10	—	1·5	0·60
205	10	—	0·5	0·20
225	10	—	0·5	0·20
245	10	—	0·5	0·20

Total loss = 3·03 per cent. Bi_2O_4 to Bi_2O_3 loses 3·30 per cent.

Hypobismuthic oxide is almost wholly reduced to bismuthous oxide by heating in carbon monoxide at 245—250°; reduction begins at about 105°.

IV. Reduction in Hydrogen. No. 1. 0·459 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
215°	10	1·75	0·39
235	10	2·25	0·46

No. 2. 0·366 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
245°	10	4	1·09
255	10	1	0·27
265	10	21	5·74

Total loss (No. 2) = 7·10 per cent. Bi_2O_4 to Bi_2O_2 loses 6·61 per cent.

Appearance of residue was black, with a few greyish specks.

Hypobismuthic oxide is therefore reduced to hypobismuthous oxide in hydrogen at about 265—270° after 30 minutes' (discontinuous) action, but bismuthous oxide is not wholly reduced to the lower oxide in hydrogen, even at 300°. (See above, Table II.)

V. Heating in Air. 0·2592 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
245°	10	1·5	0·57
255	10	0·0	0·0
265	10	0·5	0·19
275	10	1·0	0·38
285	10	0·4	0·18
295	10	2·4	0·92
305	10	2·0	0·76
315	10	0·7	0·27
325	10	0·2	0·09

Total loss = 3·36 per cent. Bi_2O_4 to Bi_2O_3 loses 3·30 per cent.

Hypobismuthic oxide is therefore reduced to bismuthous oxide by heating in air to about 325°.

VI. Heating in Oxygen. 0·249 gram taken.

Temp.	Time in mins.	Loss. in mgrms.	Percentage loss.
245°	10	2·0	0·8
255	10	0·0	0·0
265	10	2·0	0·8
275	10	1·0	0·4
285	10	2·1	0·9
295	10	1·1	0·5
305	10	0·0	0·0

Total loss = 3·4 per cent.

Hypobismuthic oxide is therefore reduced to bismuthous oxide in a current of oxygen, at about the same temperature as that at which it suffers reduction when heated in air.

0·30 gram heated at 100° for 15 minutes, and then at 140° for 15 minutes, in a slow current of ozonised oxygen, underwent no change in appearance or in weight.

Heated to 200° in oxygen, no change of weight. Therefore this oxide is not oxidised by direct action of oxygen or of ozone.

Bismuthic Oxide.

VII. Temperature of Initial Action of Carbon Monoxide (about 0·5 gram taken).

Temp.	Time in mins.	Turbidity in baryta-water.
70°	4	very faint.
80	1	faint.

Therefore reduction begins at about 75°.

VIII. Reduction in Hydrogen. 0·5875 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
105°	15	5·0	0·86
125	15	2·0	0·35
145	15	3·0	0·46
165	10	1·5	0·26
205	10	3·0	0·46
215	10	3·0	0·46
255	10	19·5	3·32

Total loss to 215° = 2·85 per cent. Bi_2O_5 to Bi_2O_4 loses 3·2 per cent.
Total loss = 6·17 per cent. Bi_2O_5 to Bi_2O_3 loses 6·4 per cent.

Therefore bismuthic is almost wholly reduced to hypobismuthic oxide, at about 215°, and to bismuthous oxide at about 255°, by heating in hydrogen.

IX. Heating in Air. 0·5117 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
135°	10	0·0	0·0
145	10	2·1	0·4
155	10	1·0	0·2
165	10	0·5	0·1
175	10	1·4	0·3
185	10	0·0	0·0
195	10	0·0	0·0
205	10	0·0	0·0
215	10	1·0	0·2
225	10	1·5	0·3
235	10	1·4	0·3
245	10	3·4	0·7
255	10	5·7	1·1

Total loss = 3·6 per cent.

X. Heating in Oxygen. 0·5545 gram taken.

Temp.	Time in mins.	Loss in mgrms.	Percentage loss.
135°	10	0·5	0·1
145	10	1·1	0·2
155	10	0·5	0·1
165	10	1·2	0·2
175	10	0·8	0·15
185	10	0·8	0·15
195	10	1·8	0·3
205	10	2·1	0·4
215	10	0·0	0·0
225	10	0·5	0·1
235	10	1·1	0·2
245	10	3·8	0·7
255	10	7·8	1·4
305	10	8·4	1·5

Total loss to 255° = 4·0 per cent. Total loss = 5·5 per cent.

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Bismuthic oxide heated in air to about 250°, or in a current of oxygen to about the same temperature, is therefore reduced to hypobismuthic oxide; heated in a current of oxygen to about 305°, it is almost wholly reduced to bismuthous oxide.

Heated in oxygen at 160° and at 200° under a pressure of 780 mm. bismuthic oxide suffered almost the same loss of weight as when heated under the ordinary pressure; therefore an additional pressure of 20 mm. mercury did not impress upon the oxide any greater stability than is possessed by it at the ordinary pressure.

12. We thought it advisable to examine the action of chlorine and bromine on the oxides Bi_2O_3 and Bi_2O_5. One of us had previously found that chlorine acts on Bi_2O_3 to give $BiCl_3$, and bromine (when heated with the oxide) to give $(BiO)_{11}O_2Br_7$ (this Journal, 1877, **1**, 24).

The oxides were subjected to the action of dry chlorine, and of dry carbonic anhydride charged with bromine vapour, in hard glass tubes. Action began between chlorine and bismuthic oxide as soon as the oxide was gently warmed; with bismuthous oxide action did not begin until a higher temperature was reached. Bromine did not act on either oxide so readily as chlorine; no distinct difference could be noticed between the readiness with which the bromine acted on the higher and on the lower oxide. The main product of the action of chlorine on bismuthous oxide was bismuthous chloride, recognised by its general properties and by estimation of bismuth; a very small quantity of the oxy-salt, $Bi_3O_2Cl_3$, already described as the product of the action of air, or nitrogen trioxide, on heated bismuthous chloride, was also formed. In the case of bismuthic oxide the products were the same, but a relatively larger quantity of the oxychloride was obtained. Bromine reacted on both oxides to form bismuthous bromide and the oxybromide formerly described as produced by heating together bismuthous oxide and liquid bromine, viz., $(BiO)_{11}O_2Br_7$. Relatively more of the oxybromide than of the oxychloride was obtained; the deoxidising action of bromine on bismuthous and bismuthic oxides is therefore not so complete, under similar conditions, as that of chlorine.

13. The following data are given as approximate only. The specific gravities were determined by weighing in pure benzene, the specific gravity of which had been determined to be 0·881 (20°):—

Specific gravity at 20° of—

Bi_2O_4 .... = 5·60, referred to water at same temperature.
Bi_2O_5 .... = 5·10 „ „
$Bi_2O_4.2H_2O$ = 5·80 „ „
$Bi_2O_5.H_2O$ = 5·75 „ „

Part II.—*On the Halogen Compounds of Bismuth.*

By M. M. Pattison Muir, G. Bernard Hoffmeister, and C. E. Robbs.

1. The only point with regard to the preparation of the chloride, bromide, or iodide of bismuth which we have to note is, that bismuthous iodide is very easily prepared in well-marked crystals by subliming together bismuth and iodine in proportions to form BiI_3. Heintz prepared the salt by subliming the constituent elements in an atmosphere of dry carbonic anhydride (*Pogg. Ann.*, **63**, 55).

A sample of the iodide prepared by the direct union of the elements contained 35·44 per cent. bismuth (theory requires 35·53). A specimen prepared three years ago, by Rammelsberg's wet method, now contained 35·31 per cent. bismuth (mean of 35·77 and 34·85 per cent.) showing that no decomposition had occurred.

An attempt was made to prepare Bi_2Br_4 by heating $BiBr_3$ in hydrogen; 0·5 gram of the salt lost only 3·6 per cent. at 220°, at which temperature sublimation of the original bromide proceeded rapidly ($BiBr_3$ to Bi_2Br_4 loses 17·7 per cent.).

Bismuthous iodide was heated in hydrogen, but no reduction occurred; the salt sublimed in hard steel-grey crystals, consisting of pure BiI_3. One specimen contained 35·54 per cent. bismuth; another, which had been repeatedly sublimed in hydrogen, 34·63 per cent.; BiI_3 requires 35·53 per cent.

2. The action of hydrofluoric acid on bismuthous oxide results, according to Berzelius, in the production of bismuth fluoride, which is soluble in water, and separates therefrom as a white powder.

We heated bismuthous oxide with aqueous hydrofluoric acid in a platinum dish, replacing the acid as it evaporated. When action had apparently ceased the liquid was decanted and evaporated on the water-bath; we thus obtained a deliquescent, crystalline, greyish-white mass, which, after drying between filter-paper, contained 62·5 per cent. bismuth.

Another specimen prepared in this way, but dried by warming over a low flame for 6—8 hours, contained 65·37 per cent. bismuth (mean of 64·80 and 65·95 per cent.). $BiF_3.3HF$ requires 64·22 per cent. bismuth. Another quantity of the same substance was heated in a closed platinum crucible till fumes of hydrofluoric acid were no longer evolved. The residue, which was a distinctly crystalline, grey, heavy powder, contained 79·2 per cent. bismuth (mean of 80·4, 79·0, and 78·1 per cent.). BiF_3 requires 78·65 per cent. bismuth. On boiling the deliquescent salt mentioned above with successive quantities of water, a heavy, white, non-deliquescent powder was obtained, which contained 86·50 per cent. bismuth; BiOF requires 85·71 per cent.

The greater part of the bismuthous oxide which was acted on by hydrofluoric acid remained as a heavy colourless powder; when this had been washed with cold water till the washings were nearly neutral, and dried at 100°, it contained 73·72 per cent. bismuth (mean of 74·0, 72·10, 73·40, and 74·42 per cent.). BiOF.2HF requires 73·69 per cent. bismuth.

When washing of the insoluble in hydrofluoric acid had been continued, with hot water, till the washings were perfectly neutral—this required about 80 or 100 washings—the residual colourless powder dried at 100° contained 85·51 per cent. bismuth (mean of 85·70 and 85·31 per cent.). BiOF requires 85·71 per cent. bismuth.

Bismuthic fluoride was also obtained, in crystalline form, by very strongly heating the double salt BiOF.2HF, mentioned above, in a closed platinum crucible for about an hour. Closely agreeing numbers were obtained on analysis.

Bismuth fluoride, BiF_3, is quite insoluble in, and is unacted on by water, is decomposed and dissolved by hot hydrochloric, sulphuric, or nitric acid, and is scarcely altered or volatilised by heating in an open platinum basin at a full red heat. The double salt $BiF_3.2HF$ is slowly decomposed by cold, more quickly by hot water, with formation of BiOF.2HF. If a little free hydrofluoric acid be present in the wash water a considerable amount of bismuth goes into solution.

The final product of the action of aqueous hydrofluoric acid on bismuthous oxide is bismuthyl fluoride; bismuth fluoride is, however, much more stable towards water and towards heat than any of the other halogen compounds of bismuth.

3. It has been before shown that bismuthous iodide is much more stable towards oxidising agents and towards water than the corresponding chloride or bromide (this Journal, Trans., 1878, 192). The results of the experiments to be described exhibit this greater stability.

About 0·5 gram of bismuthous iodide was shaken up with cold water in the proportion of 3,000 mols. H_2O to 1 mol. BiI_3 for 30 and for 60 minutes, when the solution was filtered, and hydriodic acid determined in the filtrate:—

BiI_3 *prepared in Wet Way.*

Percentage decomposition after 30 minutes = 13·3
" " 60 " = 24·3

BiI_3 *prepared in Dry Way.*

Percentage decomposition after 30 minutes = 17·4
" " 60 " = 19·9

Under similar conditions $BiCl_3$, or $BiBr_3$, would be entirely decomposed to BiOCl, or BiOBr. The complete decomposition into BiOI, by

heating with water, of crystalline bismuthous iodide prepared "in the dry way" is much less readily effected than the decomposition of the iodide prepared "in the wet way."

The action of N_2O_3 on bismuthous chloride and bromide has been shown to result in the production of the oxy-salts $Bi_3O_2Cl_3$ and $Bi_8O_{15}Br_6$ respectively. About 5 grams of BiI_3 (prepared in the wet way) were heated in a **V**-tube in a current of dry N_2O_3 (prepared by heating starch with nitric acid). Action began before the salt sublimed, iodine was evolved, and a crystalline sublimate, which on examination and analysis proved to be BiI_3, collected in the cold part of the tube and in a long attached exit-tube. About 0·3 gram (6·0 per cent. of the iodide used) of a red substance remained in the bend of the **V**-tube when the action was finished; this gave a slight red milkiness when boiled with water, but the greater part was unacted on; it contained 56·50 per cent. bismuth; BiOI requires 59·50 per cent.

Bismuthous iodide is evidently much less fully decomposed by N_2O_3 than the corresponding chloride and bromide. The oxidised product of the action is BiOI, which is also produced by slowly subliming the iodide in air; no tendency to form complex oxyiodides corresponding to, or analogous with, the complex oxychlorides or bromides, appears to exist.

When sulphur is heated with bismuthous chloride, sulphobismuthyl chloride, (BiSCl), is produced. Bismuthous bromide and sulphur were heated in a subliming vessel in molecular proportions; much sulphur vapour was given off, crystals of bismuthous bromide sublimed, and a reddish crystalline mass remained, containing 47·44 per cent. bismuth and 51·30 per cent. bromine (mean of 47·17 and 47·60, and of 51·08 and 51·52 respectively), which does not differ much from the numbers required for $BiBr_3$, viz., bismuth 46·66, and bromine 53·53 per cent. The substance contained a little sulphur; it was readily decomposed by water, yielding a nearly white, apparently crystalline body, which contained 22·38 per cent. bromine and a little sulphur; BiOBr requires 26·11 per cent. bromine.

These results show that bismuthous bromide is scarcely decomposed by sublimation in contact with sulphur, or if decomposed, that the sulphobromide formed is again easily resolved into its constituent substances; hence BiSCl is a more stable salt than BiSBr, if the latter exists.

When bismuthous iodide and sulphur were heated together both substances sublimed unchanged; sulphur-vapour therefore has no action on vapour of bismuthous iodide.

The oxyhaloïd salts of bismuth, as is usually the case, are more stable than the sulphohaloïd salts. When dry sulphur dioxide is passed over hot bismuthous bromide no action ensues; it has been

before shown that neither is bismuthous chloride decomposed by this gas; it seemed unnecessary to make an experiment with bismuthous iodide, undoubtedly it would be unaltered by the action of hot sulphur dioxide.

No action is exerted by dry carbonic anhydride on heated bismuthous bromide.

4. It is stated in *Roscoe and Schorlemmer's Chemistry* that bismuthyl iodide when sublimed in air is resolved into a crystalline oxide. We find that only a very small quantity of this salt is decomposed, with formation of Bi_2O_3, by heating even in an open vessel for some days.

5. Another attempt (see this Journal, 1877, **2**, 136) was made, but only with negative results, to prepare a chlorobromide of bismuth by passing carbonic anhydride charged with bromine vapour over hot bismuthous chloride contained in one bend of a **W**-tube, the other limb being surrounded by a freezing mixture: no action occurred, the second limb contained liquid bromine only.

6. The final distribution of salts when bismuthous oxide is acted on by aqueous hydrochloric acid has been shown by one of us (No. II of these "Contributions") to be represented by the symbols on the right hand side of the equation—

$$Bi_2O_3 + 2HCl + xH_2O = 2BiOCl + (x + 1)H_2O.$$

We have now examined the distribution of salts which occurs when the same oxide is acted on by aqueous hydriodic acid, and find that it is not quite analogous to that just described; the reaction may be formulated thus:—

$$Bi_2O_3 + 6HI + xH_2O = 2BiI_3 + (x + 3)H_2O.$$

If, however, x be made very large relatively to the amount of HI present, if the temperature be raised, or if the changing system be exposed to the action of direct sunlight, BiOI is produced.

The reaction which occurs when aqueous hydriodic acid is added to bismuthyl chloride on the one hand, and aqueous hydrochloric acid to bismuthyl iodide on the other, may be thus expressed:—

$$3BiOCl + xHI + x'H_2O = 2BiI_3 + BiCl_3 + (x - 6)HI + (x' + 3)H_2O.$$

$$4BiOI + xHCl + x'H_2O = 3BiCl_3 + BiI_3 + (x - 9)HCl + HI + (x' + 4)H_2O.$$

The amount of change in a given time in the first reaction may be greatly decreased by adding a large quantity of water, whereby the $BiCl_3$ is reconverted as soon as produced into BiOCl: unless the value of x' be very large in this reaction little or no BiOI is produced. In the second reaction the course of the change may be modified by

making x' very large; the $BiCl_3$ produced is thus partly decomposed, and a secondary reaction occurs between the BiOCl thus produced and HI set free in the primary change, in accordance with the first of the two equations given above.

The actions which occur between the components of a system comprising $BiCl_3$, BiI_3, BiOCl, BiOI, HCl, HI, and H_2O mols., is thus seen to be very complex; the final equilibrium is conditioned chiefly by the relative quantities of the salts (largely the quantity of H_2O), and by the temperature: inasmuch as BiI_3 is more stable than $BiCl_3$ the iodide tends to be produced in relatively large quantities. Thermal measurements would undoubtedly throw much light on these phenomena of equilibrium: most probably the "heat of formation" of BiI_3 is greater than that of $BiCl_3$, and the difference between the "heats of formation" of $BiCl_3$ and BiOCl greater than that between the "heats of formation" of BiI_3 and BiOI.

7. The following numbers are given as approximate only. The specific gravities were determined by weighing in benzene:—

Specific gravity of $BiBr_3$ at 20° = 5·4, referred to water at 20°.
" " BiOBr " = 6·7 " "
" " BiOCl " = 7·2 " "

Specific gravity of BiI_3 is given in text-books as 4·56, and of $BiCl_3$ as 5·65.

V.—*On a New Class of Colouring-Matters from the Phenols.*

By Raphael Meldola.

In a preliminary note published last year (*Ber.*, 1879, 2065) I pointed out the existence of a new class of bodies formed by the action of nitroso-dimethylaniline on phenols not containing a methyl-group. The mode of performing the reaction is described in the note referred to, and need not be here repeated.

Preparation of Nitroso-dimethylaniline.

The following method of preparing this substance, which is based on the insolubility of the nitrate in alcohol, will I think be found more advantageous than that of Baeyer and Caro (*Ber.*, **7**, 1074, 809 and 963), especially in cases where large quantities are required, as it dispenses with the use of amyl nitrite:—

50 parts by weight of dimethylaniline are mixed with an equal

weight of hydrochloric acid and 200 parts of alcohol, the mixture being well cooled by immersing the vessel in iced water. A standard solution of sodium nitrite containing the necessary quantity of this salt is then gradually stirred in, and the mixed solutions allowed to stand for about half an hour, after which the theoretical quantity of nitric acid necessary to convert the nitroso-compound into nitrate is gradually poured in. The nitric acid must be diluted with its own volume of alcohol, and cooled in ice before being added to the other solution. In a short time the crystals of the nitrate begin to separate out, and in about 30 minutes the solution solidifies to a pasty mass, which must be collected on a vacuum-filter, washed once or twice with alcohol, and finally with alcohol-ether. The dried nitrate can easily be converted into the free base in the usual manner; by agitating with dilute NaHO and ether, and separating the ethereal solution of the base. On distilling off the ether, the nitroso-dimethylaniline is obtained in the usual form, the yield being from 60 to 70 per cent. of the theoretical quantity.

β-Naphthol Violet.

Specimens of the hydrochloride of this substance prepared in the manner already described, after purification by several crystallisations from alcohol, gave the following results on analysis :—

I. 0·5930 gram dried *in vacuo* over H_2SO_4 gave 1·4987 gram CO_2 and 0·2943 gram H_2O.

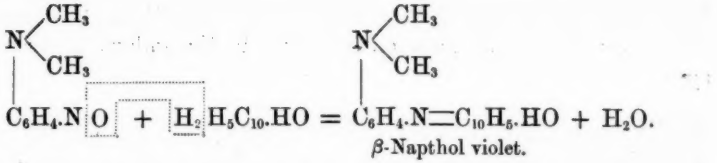
II. 0·3160 gram gave 0·8042 gram CO_2 and 0·1525 H_2O.

III. 0·2158 gram gave 0·0968 AgCl.

IV. 0·3324 gram gave 0·1518 AgCl.

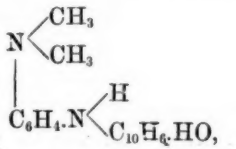
Theory for N $\left\{\begin{matrix}(CH_3)_2\\C_6H_4.N\end{matrix}\right.$: $C_{10}H_5.HO,HCl$.			Theory. I.	II.	III.	IV.	(Mean).
C_{18} ..	216	69·12	68·92	69·40	—	—	69·16
H_{17} ..	17	5·44	5·51	5·35	—	—	5·43
N_2 ..	28	8·96	—	—	—	—	—
O ..	16	5·12	—	—	—	—	—
Cl ..	35·5	11·36	—	—	11·09	11·29	11·19
	312·5	100·00					

These results show that when nitroso-dimethylaniline acts upon a phenol not containing the methyl-group the oxygen of the nitroso-group directly attacks the aromatic nucleus of the phenol in accordance with the equation—



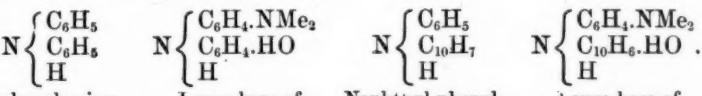
β-Napthol violet.

The hydrochloride of β-naphthol violet forms large bronzy needles, readily soluble in hot water and alcohol, and much resembling potassium permanganate in appearance. The aqueous solution has an intense violet colour, which is changed to a deep blue on adding an excess of strong sulphuric acid. The nitrate and sulphate form small bronzy-green needles. By the action of reducing agents a colourless leuco-base is obtained, which I have been unable to isolate, owing to the great readiness with which it oxidises, a few minutes' exposure to the air causing the regeneration of the violet colouring-matter. This leuco-base can, however, only have the formula—



according to which two atoms of hydrogen are required for its production.*

It is of theoretical interest to note that the leuco-bases of these colouring-matters may be considered as derivatives of diphenylamine, naphthyl-phenylamine, &c. Thus—

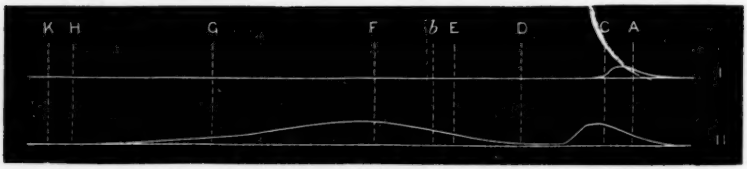


Diphenylamine. Leuco-base of phenol colour. Naphthyl-phenyl-amine. Leuco-base of naphthol violet.

Although β-naphthol violet possesses great intensity of colour when in solution, it is not readily taken up by silk or wool, and is not, therefore, of much value as a dye-stuff. By properly adjusting the strength of the bath and using the acetate of the base, it can, however, be made to gradually dye these fabrics. It thus imparts to silk a dull violet colour, and to wool a deep shade of indigo-blue. A strong solution of the colour (either aqueous or alcoholic) appears red

* My friend, Mr. R. J. Friswell, at my request, was good enough to confirm this statement, by reducing a standard solution of the violet with stannous chloride. The reaction did not readily take place in the cold, but on adding the stannous chloride solution to that of the violet, and boiling the latter after each addition, results were obtained which sufficiently accorded with the theory.

by transmitted light, and changes to violet on dilution. The cause of this dichroism will be seen on referring to the following absorption spectra:—



I. 0·1 gram in 500 c.c. water.
II. 0·1 gram in 6,000 c.c. water.
Solution in tube 16 millim. in diameter.

The free base can readily be obtained from β-naphthol violet by decomposing any of its salts with an alkaline carbonate, when it is thrown down as a dark flocculent powder, which dissolves in benzene with a red colour when dry, but is not easily crystallisable. The hydrochloride is completely precipitated from its alcoholic solution by $PtCl_4$, the double salt forming microscopic bronzy crystals.

The corresponding colours from phenol, resorcinol, and α-naphthol have been prepared, but, owing to the difficulty of obtaining them in a crystalline form, their investigation is not yet completed.

VI.—*On Nitroso-β-Naphtholsulphonic Acid.*

By Raphael Meldola.

The ideas which have prompted the investigation which has led to the discovery of this nitroso-sulphonic acid are briefly as follow:—

The colouring-matters described in the preceding paper are, as already stated, of but little value as dye-stuffs, and it therefore became of interest to investigate the derivatives of these bodies containing acid radicles, it being now well known that the tinctorial value of the "diazo-colours" is greatly increased by the introduction of one or more such radicles into one or both of the aromatic nuclei linked together by the diazo-group. As the "β-naphthol violet" did not appear to readily form a sulphonic acid by the direct action of sulphuric acid upon it, I was led to investigate the action of nitrous acid upon the sulphonic acids of the naphthols, with a view to producing by this means the nitroso-sulphonic acids, which would furnish a

means of forming bodies of the type of the "β-naphthol violet" containing the group HSO_3.

When a solution of sodium nitrite is mixed with a solution of a salt of β-naphtholsulphonic acid, the two salts being in exact molecular proportions, on adding dilute HCl to the well-cooled mixture, a solution of a deep orange colour is formed, and no trace of nitrous gas is evolved. These facts led me to believe that some definite reaction had taken place, and on adding to the orange solution a large excess of caustic soda a green colour was produced, and on standing in the cold for some time, minute green needles of the sodium salt of nitroso-β-naphtholsulphonic acid separated out. The extreme solubility of this sodium salt in water, the readiness with which it decomposes on evaporating the solution on a water-bath, and the difficulty of isolating in a state of purity a substance requiring excess of caustic soda for its precipitation, led me to seek for some other method of obtaining a salt fit for analysis. This process, which will be described later on, is based upon the insolubility of the Ba or Ca salt of the new acid.

The β-naphtholsulphonic acid employed in these experiments was prepared from commercial β-naphthol purified by distillation and crystallisation from toluene till it possessed a melting point of 122°. This β-naphthol was mixed with about 2—3 times its weight of strong sulphuric acid, and heated on a water-bath for about half an hour. As the free acid was not required, the contents of the flask were poured into a large bulk of water, neutralised with milk of lime, boiled, and filtered. The calcium salt was then converted into the ammonium salt by decomposition with ammonium carbonate and filtering off the calcium carbonate. The filtrate on cooling deposits a certain amount of the ammonium salt, and a further quantity can be obtained by evaporating the mother liquor. The ammonium salt was chosen because of the readiness with which it crystallises, and the ease with which it can thus be obtained in a state of perfect purity.

Ammonium β-naphtholsulphonate crystallises in long flat transparent prisms with pointed extremities, or, when a large bulk of the solution is allowed to cool slowly, in large plates sometimes half an inch in length. Analysis showed it to possess the formula $C_{10}H_7.HO.NH_4SO_3$. At 24° 100 parts of water dissolve nearly 3 parts of the salt. The latter is very stable, and can be boiled with dilute sulphuric or hydrochloric acid without parting with its ammonium group.

Barium Nitroso-β-Naphtholsulphonate.

To prepare this salt 16—18 parts of distilled water are poured upon one part of the finely powdered ammonium salt, and a standard solu-

tion of sodium nitrite added in the proportion of one molecule of the latter salt to one of the sulphonate. Dilute hydrochloric acid is then gradually poured into the well-cooled solution till it shows a strongly acid reaction, and all the ammonium salt has dissolved. The deep orange solution is then made alkaline with ammonia, and barium chloride solution added as long as a precipitate forms. The latter is collected on a filter, where it remains as a bright green paste, which is well washed, first with cold and finally with boiling water, till a few drops of the filtrate no longer give a crimson colour on the addition of dilute hydrochloric or sulphuric acid. The green paste is then transferred to a flask and agitated with dilute hydrochloric acid, which changes its colour to orange, and on standing for some time a heavy crystalline deposit settles down, which is collected and washed with cold water. Both the green paste and orange crystals are barium salts of nitroso-β-naphtholsulphonic acid, and will be designated by their respective colours. The orange salt may be purified by two or three crystallisations from boiling water, or, in cases where there is much associated impurity, the hot aqueous solution may be precipitated by ammonia, and the green salt collected, washed, and again converted into the orange salt by dilute hydrochloric acid, and recrystallised.

Analyses of Orange Ba *salt.*

I. 0·4944 gram dissolved in hot water and decomposed by H_2SO_4 gave 0·1742 gram $BaSO_4$.

II. 0·5914 gram gave 0·2097 gram $BaSO_4$.

III. 0·3309 „ 0·1168 „

IV. 0·8440 gram fused with KHO and KNO_3 gave 0·5852 gram $BaSO_4$.

V. 0·3675 gram fused as above gave 0·2670 gram $BaSO_4$.

VI. 0·2951 gram dried at 100°, burnt with lead chromate gave 0·0632 gram H_2O (1 mol. of water of crystallisation subtracted) and 0·3930 gram CO_2.

Water of Crystallisation.

VII. 0·7153 gram dried at 100°, and heated in an air-bath to 140—150° till the weight was constant, lost 0·0171 gram H_2O.

VIII. 0·6453 gram treated as above lost 0·0168 gram H_2O.

		Theory.	Found (mean).
C_{20}	240	36·41	36·32
H_{12}	12	1·82	2·37
N_2	28	4·25	—
O_{10}	160	24·30	—
S_2	64	9·71	9·74
Ba	137	20·78	20·76
H_2O	18	2·73	2·49
	659	100·00	

These results show that the orange salt has the formula:—

$$\begin{matrix} C_{10}H_5.HO.NO.SO_3 \\ C_{10}H_5.HO.NO.SO \end{matrix} > Ba, H_2O.$$

A determination of Ba in a specimen of the anhydrous salt dried at 140—150° gave 21·33 per cent.; theory requiring 21·37.

The orange salt crystallises in large tufts of flattened needles with a golden lustre, crystals nearly three-quarters of an inch long having sometimes been obtained by the slow crystallisation of a large bulk of the solution. It is but very sparingly soluble in cold water; at 30° 100 parts of water dissolve about two parts of the salt.

The green Ba salt was prepared for analysis by dissolving the orange salt in a considerable quantity of hot water, and adding ammonia. The bright green bulky precipitate thus obtained was seen under the microscope to consist of minute needle-shaped crystals. Analysis showed it to possess the formula:—

$$C_{10}H_5.NO < \begin{matrix} O \\ SO_3 \end{matrix} > Ba, 2H_2O.$$

The action of an alkali upon the orange salt is therefore represented by the equation:—

$$(C_{10}H_5.NO.HO.SO_3)_2Ba + NH_4HO = C_{10}H_5.NO < \begin{matrix} O \\ SO_3 \end{matrix} > Ba + C_{10}H_5.NO.HO.NH_4SO_3 + H_2O.$$

The ammonium nitroso-β-naphtholsulphonate formed in this reaction is most obstinately retained by the green Ba salt, so that for the purposes of analysis it was found necessary to add sufficient $BaCl_2$ to the ammoniacal solution to decompose the whole of the ammonium salt present. The green salt is then collected and well washed with boiling water, in which it is practically insoluble.

Analysis of Green Ba *Salt.*

I. 0·370 gram (dried at 100°) gave on decomposition with dilute H_2SO_4 0·2039 gram $BaSO_4$.

II. 0·6156 gram fused with KHO and KNO_3 gave 0·3396 gram $BaSO_4$.

III. 0·3029 gram (dried at 100°) burnt with lead chromate gave 0·3153 gram CO_2 and 0·0422 gram H_2O (water of crystallisation subtracted).

Water of Crystallisation.

IV. 0·5198 gram dried at 100°, and in an air-bath to 240—250° till the weight was constant, lost 0·0438 gram H_2O.

V. 0·4056 gram treated as above lost 0·0354 gram H_2O.

	Theory.		Found.
C_{10}	120	28·30	28·39
H_5	5	1·17	1·54
N	14	3·30	—
O_5	80	18·88	—
S	32	7·55	7·37
Ba	137	32·31	32·37
$2H_2O$	36	8·49	8·57 (mean)
	424	100·00	

The water of crystallisation is not given off completely till the salt is heated to the temperature mentioned above (240—250°), when partial decomposition takes place, but the weight remains constant as long as this temperature is not exceeded.

Nitroso-β-naphtholsulphonic acid thus forms two classes of salts represented by the green and orange Ba salts. In cases where large quantities of a salt of this acid are required, calcium chloride can be used for precipitating the ammoniacal solution of the acid after its first formation from ammonium β-naphtholsulphonate by the action of nitrous acid ($NaNO_2$ and HCl).

By decomposing a solution of the Ba salt with an equivalent quantity of H_2SO_4 and evaporating the solution in a vacuum, the free acid was obtained in microscopic orange nodular crystals, extremely soluble in water, and decomposed by heating to a very moderate temperature in a dry tube, so that its melting point could not be determined.

Of the other salts of nitroso-β-naphtholsulphonic acid I have prepared the following:—

Silver ammonium (double) *salt* formed by adding $AgNO_3$ to a solution of the ammonium salt of nitroso-β-naphtholsulphonic acid in the presence of an excess of ammonia. Dull olive-green microscopic needles decomposed by boiling water. Analysis gave the formula:—

$$C_{10}H_5.NO.NH_4O.AgSO_3 + C_{10}H_5.NO.NH_4O.NH_4SO_3 + H_2O.$$

Found, 15·87 per cent. Ag, 9·69 per cent. S; theory, 15·83 per cent. Ag, 9·38 per cent. S.

Magnesium salt, formed by decomposing the orange Ba salt with an equivalent (2 mols.) of $MgSO_4$, and adding ammonia to filtrate. Dull orange needles moderately soluble in cold, readily soluble in boiling, water. Analysis gave the formula:—

$$C_{10}H_5.NO<\begin{matrix}O\\SO_3\end{matrix}>Mg,3H_2O.$$

Found, 7·27 per cent. Mg, 16·70 per cent. H_2O; theory, 7·29 per cent. Mg, 16·41 per cent. H_2O. Water of crystallisation not given off till 250°.

Zinc salt, formed in the same manner as the Mg salt. Large scaly crystals, dull green by reflected light, orange by transmitted light. Moderately soluble in cold water, more readily soluble in hot water. Analysis gave the formula:—

$$C_{10}H_5.NO<\begin{matrix}O\\SO_3\end{matrix}>Zn,3H_2O.$$

Found, 17·81 per cent. Zn, 8·86 per cent. S, and 14·62 per cent. H_2O; theory, 17·56 per cent. Zn, 8·64 per cent. S, 14·59 per cent. H_2O. Water of crystallisation only given off completely at 280° with partial decomposition of the salt.

Lead salt precipitated on adding a solution of lead acetate to a solution of the sodium or ammonium salt of nitroso-β-naphtholsulphonic acid acidulated with acetic acid. Minute ochreous needles insoluble in boiling water. Analysis gave the formula:—

$$C_{10}H_5.NO<\begin{matrix}O\\SO_3\end{matrix}>Pb,H_2O.$$

Found, 43·60 per cent. Pb; theory, 43·48 per cent. Pb. No loss of water at 250°.

Copper Salts.—On adding a solution of $CuSO_4$ to a solution of the free nitroso-sulphonic acid containing an excess of H_2SO_4, a bulky brown gelatinous precipitate, almost insoluble in boiling water, separates out. On suspending this gelatinous salt in cold water and adding ammonia a double copper-ammonium salt settles down after some hours in the form of small brown glistening scales. The constitution of this salt has not been determined. Analysis gave 17·92 per cent. Cu and 8·55 per cent. S.

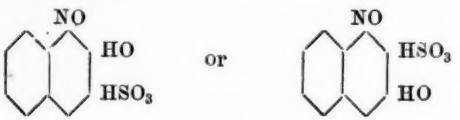
An attempt was made to prepare an acetyl derivative of nitroso-β-naphtholsulphonic acid by acting upon the sodium salt of acetyl-β-naphtholsulphonic acid with sodium nitrite and dilute hydrochloric acid, but the acetyl-group appears to be eliminated in the course of the reaction, as on adding ammonia and barium chloride the ordinary

green Ba salt was precipitated. An attempt to prepare a nitroso-derivative of methyl-β-naphthol in a similar manner was also unsuccessful.

Nitroso-β-naphtholsulphonic acid is very easily decomposable. The nitroso-group is readily reducible by any reducing agent, but I have not yet been able to obtain the corresponding nitro-sulphonic acid, either by the action of dilute nitric acid or of an alkaline solution of potassium ferricyanide, the molecule apparently completely breaking up under the action of these reagents. On agitating a solution of the nitrososulphonic acid with 1 mol. of bromine the latter is absorbed, but no definitely crystalline brom-nitroso acid was separable.

Constitution of Nitroso-β-Naphtholsulphonic Acid.

I have made numbers of experiments with a view to determine the constitution of this acid. The free acid when repeatedly evaporated with dilute nitric acid gave no phthalic acid, neither did the nitroso- nor amido-acids when oxidised with an alkaline solution of potassium permanganate. Phthalic acid was, however, obtained by repeatedly evaporating the amido-acid with dilute nitric acid. This result is of interest as showing that in nitroso- and amido-β-naphtholsulphonic acid all these substituents are in the same benzene-ring. In their recently published monograph upon naphthalene Reverdin and Nölting ("Ueber die Constitution des Naphtalins und seiner Abkömmlinge," Genf., 1880, p. 25) assign to β-naphtholsulphonic acid a formula in which the HSO_3 and HO-groups are in different benzene-nuclei, but no reasons are assigned for adopting this constitution. In a communication to this Society last November Armstrong gave reasons for believing that in this acid the two substituents are both in the same benzene-ring, being in the two β-positions. Although I have made repeated attempts to confirm this view by oxidising β-naphtholsulphonic acid with an alkaline solution of permanganate, I have not succeeded in obtaining phthalic acid from this compound. The production of phthalic acid, however, from amido-β-naphtholsulphonic acid in the manner above described goes to support Armstrong's view of the constitution of this sulphonic acid, and shows that the nitroso-acid has the constitution:—



Among the reactions of nitroso-β-naphtholsulphonic acid which I have investigated the most interesting appears to be that with the phenols and certain primary and secondary monamines. The phenol or amine is dissolved in glacial acetic acid, the finely powdered barium or calcium salt of the nitroso-acid added, and after the addition of a small quantity of sulphuric acid the mixture is warmed. The following colouring-matters have been obtained in this manner:—

Resorcinol and ordinary *phenol* give a deep blue, changing to red on dilution with water.

Diphenylamine gives a similar blue, which retains its colour on dilution, but becomes red on neutralising with an alkali.

Benzyl-α-naphthylamine gives a fine red, which is not changed by dilution.

These bodies are probably built on the type of the β-naphthol-violet described in the last paper, and containing HSO_3 in the naphthalene-group. Their value as dyes does not appear, however, to be increased by the presence of the acid radicle. I hope to investigate these substances more fully at a future period.

On mixing solutions of ammonium nitroso-β-naphtholsulphonate and ammonium sulphite, and allowing the mixture to stand for some hours in the cold, white scaly crystals separate out, which have not yet been further investigated.

Amido-β-naphtholsulphonic Acid.

This acid was prepared by boiling a solution of the nitroso-acid with tin and hydrochloric acid, removing the tin by sulphuretted hydrogen and evaporating the cold solution in a vacuum. The acid then separates out in the form of long white needles, which after one or two washings with cold water are sufficiently pure for analysis:—

0·2380 gram fused with KHO and KNO_3 gave 0·2380 gram $BaSO_4$ = 13·73 per cent. S.

0·4984 gram gave 0·4928 gram $BaSO_4$ = 13·57 per cent. S.

	Theory for $C_{10}H_5.NH_2.HO.HSO_3$.	Found (mean).
S.....	13·38	13·65

Amido-β-naphtholsulphonic acid is readily soluble in water. Its aqueous solution, and especially that of its salts, oxidises on exposure to the air, and turns brown. A hot solution undergoes this change rapidly. The melting point of the acid could not be determined, as it decomposes on heating.

In concluding this paper I may take the opportunity of announcing that I have recently succeeded in obtaining an iodine derivative of β-naphthol by acting upon this substance dissolved in glacial acetic

acid with iodine in the presence of lead acetate. I hope shortly to lay before the Society an account of this substance and some of its derivatives. It is also my pleasing duty to express my thanks to the firm of Brooke, Simpson, and Spiller, in whose laboratory at the Atlas Works these investigations have been conducted.

VII.—*Note on the Formation of Carbon Tetrabromide in the Manufacture of Bromine.*

By J. C. Hamilton, Student in the Yorkshire College, Leeds.

A quantity of a white crystalline substance which had been obtained as a residue after the distillation of a quantity of commercial bromine was given to me by Professor Thorpe, with the request that I would ascertain its nature and composition. From its physical properties Dr. Thorpe was of opinion that it was carbon tetrabromide, a supposition which my analysis has confirmed. It had the characteristic smell of this compound, melted at 90·1°, and solidified at 88·6°. Recrystallisation from alcohol made no appreciable alteration in the fusing point. Boiled with an alcoholic solution of soda it was at once decomposed, with formation of a white precipitate of sodium bromide, which readily dissolved on addition of water. On acidulating the liquid with nitric acid and adding silver nitrate, silver bromide was formed. An analysis made by means of this decomposition yielded the following results:—

0·3424 gram gave 0·7754 AgBr and 0·0036 Ag = 97·1 per cent. Br.
Carbon tetrabromide contains 96·4 per cent. Br.

The formation of this body in the manufacture of bromine has not hitherto been noticed. It is probably formed by the action of the halogen on the organic matters derived from the sea-weed from which the bromine made in this country is procured.

VIII.—COMMUNICATIONS FROM THE LABORATORY OF THE UNIVERSITY COLLEGE, BRISTOL.

1. *On the Volume of Sodium at its Boiling Point.*

By W. Ramsay, Ph.D.

University of Bristol

The method applied to the determination of the specific gravity of sulphur at its own boiling point, and described in the *Chemical Society's Journal*, 1879, p. 471, was extended with slight modifications to metallic sodium. The vessel containing the sodium consisted of an iron tube, contracted to a narrow orifice at the top, and communicating with a narrow iron tube at the lower end; the narrow tube was bent twice at right angles, so that its extremity was level with the orifice at the top of the wider tube; in fact it was as near an approach in form to the apparatus used for the specific gravity of boiling sulphur as the difference in properties of iron and glass would allow.

A cast-iron vessel was used as the bath for sodium vapour. After the iron "bulb" had been filled with liquid sodium it was suspended in the cast-iron pot, and about half an ounce of sodium was placed in the pot. An iron cover, through which a small hole had been drilled, was luted on to the pot. The heat of a charcoal fire was employed to volatilise the sodium. After the metal had been boiling briskly for about ten minutes, and its vapour had been burning at the orifice in the lid, the cover was lifted off; the iron "bulb" was withdrawn and plunged into heavy paraffin oil while still red-hot, and after cooling it was freed from oil and weighed.

The following data were obtained:—

Capacity of iron "bulb" 6·61 c.c.
Weight of sodium at its own boiling point filling bulb 4·90 grams.
Specific gravity of sodium at its own boiling point = 0·7414.
Specific volume (reciprocal of specific gravity) = 1·349.
Specific volume multiplied by atomic weight (atomic volume) = 31·0.

This number represents the volume of liquid sodium at its boiling point condensed from 11,163 volumes of gaseous sodium, assumed to exist at 0°.

This result, from the method employed, can lay claim to only a rough approximation to correctness, for it is evidently influenced by the expansion of the iron vessel, the oxidation of the sodium, and the difficulty of working at such a high temperature. It would appear,

however, from this experiment that the coefficient of expansion of sodium is not high, since between the ordinary temperature and its boiling point it expands only from 1 to 1·331.

2. *On the Volume of Bromine at its Boiling Point.*

Four determinations by the method described in the *Journal of the Chemical Society*, 1879, p. 471, gave the following results:—

	Specific gravity.	Specific volume.	Atomic volume.
1.	2·9503	0·3390	27·12
2.	2·9474	0·3393	27·14
3.	2·9483	0·3392	27·13
4.	2·9471	0·3393	27·15

Mean specific gravity, 2·9483.
Mean specific volume, 0·3392.
Mean atomic volume, 27·135.

The bromine used for this experiment was distilled with strong sulphuric acid and manganese dioxide to free it from water and hydrobromic acid, and with potassium bromide to remove any trace of chlorine which might have been present. The number obtained is somewhat in excess of that given by Thorpe, viz., 26·74.

3. *On the Volume of Phosphorus at its Boiling Point.*

By D. Orme Masson, M.A., B.Sc., and W. Ramsay, Ph.D.

The apparatus was very similar to that used by one of us in determining the density of sulphur under the same circumstances. It will therefore be necessary to describe the difference only. The phosphorus was melted in a wide tube through which a stream of dry carbonic anhydride passed, and the bulb, which was connected with a tube passing through the cork, was filled by suction. When cold it was reversed, so that the two capillary openings were uppermost, and the phosphorus in the wide tube was boiled by the heat of a sand-bath. When liquid phosphorus had ceased to expand and flow out from the capillaries the operation was stopped, and the bulb, the capacity of which had been previously ascertained, was cooled, cleaned externally with carbon disulphide, and weighed.

The mean results of four experiments were as follows:—

Specific gravity	1·4850
Specific volume	0·6734

Specific volume × atomic weight = 20·91, with a probable error of ± 0·3987 on the mean result.

4. *Discussion of Results.*

These observations add two to the number of elements the atomic volumes of which have been determined in the free condition. Comparison of the values, in the elementary and combined states, is given in the following table:—

	Free.	Combined.
Br.....	27·135	28·1
S	21·60	22·6 and 28·6
P	20·91	25·3
Na.....	31·00	(?)

The numbers obtained by Thorpe (*Chem. Soc. Jour.*, 1880, 385) for bromine in combination are in $CHBr_3$, 29·0; in $POBrCl_2$, 28·7; in PBr_3, 27·7; in $CBrCl_3$, 29·4; in $C_2H_4Br_2$, 26·7; and in CH_2BrCl, 29. The mean result is the one given in the above table. The values for combined sulphur are those given by Kopp. Ramsay found (*loc. cit.*) the same values as those of Kopp in CS_2, and 22·65 in S_2Cl_2, assuming the value of chlorine to be 22·8.

The value of combined phosphorus is the mean of ten estimations, varying between 24 and 26·1. The value of sodium in combination has not as yet been determined.

It is evident that the atomic volume of bromine is the same (or nearly the same), whether it be taken in the free or the combined condition, viz.:—

Free ..... 27·135 Combined .... 28·10

This is to be expected, as the halogens have only one atomic volume when in combination. Turning to sulphur, we find the value in the free state to be nearly identical with the lower of the two values which it possesses in combination.

The element nitrogen, which is closely allied to phosphorus, is known to possess various atomic volumes, according as it exists in amines, members of the pyridine series, and in combination with carbon as cyanogen or nitriles, or with oxygen, as the nitro-group. It is therefore not at all unlikely that phosphorus possesses more than one value.

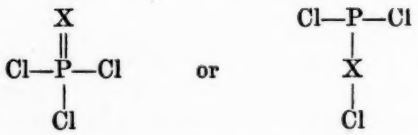
The value of phosphorus has been deduced from the following determinations by Pierre, Buff, and Thorpe (Thorpe, *Chem. Soc. J.*, *loc. cit.*), which it is necessary to review in their order:—

1. PCl_3, 93·3; P = 25·2, Cl being taken as 22·7.
2. PBr_3, 108·3; P = 24·0, Br being taken as 28·1.
3. $PCl_2(C_2H_5O)$, 128·6; P = 25·9, Cl having the previous value

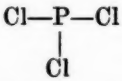
assigned to it, and Kopp's values (C = 11, H = 5·5, and O = 7·8) being assumed for the elements of the alcoholic group.

4. $POCl_3$, 101·4; P = 25·5, O = 7·8, Cl as before.
5. $PSCl_3$, 116·1; P = 25·4, S = 22·6, Cl as before.
6. $POBrCl_2$, 107·4; P = 26·1, O = 7·8, Br and Cl as before.

On what grounds are the values 7·8 and 22·6 assigned to oxygen and sulphur respectively in the last three compounds? So far as we can judge, the only reason is that a uniform value may be assigned to phosphorus in all its compounds. From general considerations, POCl and $PSCl_3$ must have one of the following constitutional formulæ:—



where X stands for O or S. PCl_3, on the other hand, can only be represented by the formula:—



If the second formula be assigned to $PXCl_3$ then phosphorus remains a triad, and would naturally have the same value as in PCl_3, but if the former formula represents the constitution of the body then phosphorus becomes a pentad. In this case there is likelihood that phosphorus should have two values, one in the PCl_3 type of compound, and another in the PCl_5 type. Moreover, oxygen has been proved to have the value 12·2 when attached by both bonds to the same atom, instead of 7·8, as it has in hydroxyl and similar groups.

Supposing then that the formula is $XPCl_3$, the value of phosphorus may be calculated in the following manner:—

(The numbers are those of the above determinations.)

4. Molecular volume of $POCl_3$	101·4
Less (O = 12·2 + Cl_3 = 68·1)	80·3
Atomic volume of phosphorus.....	21·1
5. Molecular volume of $PSCl_3$	116·1
Less (S = 28·6 + Cl_3 = 68·1)	96·7
Atomic volume of phosphorus.....	19·4
6. Molecular volume of $POBrCl_2$	107·4
Less (O = 12·2 + Cl_2 = 45·4 + Br = 28·1)	85·7
Atomic volume of phosphorus.....	21·7

The mean of these results is 20·7.

On comparing this with the atomic volume of free phosphorus, it is evident that the two numbers are identical:—

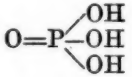
	Free.	Combined.
Phosphorus	20·9	20·7

The arguments for this value are—(1), that there is much more probability that $POCl_3$ has the formula $OPCl_3$ than $P(OCl)Cl_2$, for it is obtainable from the pentachloride by a direct simple reaction; (2), that bromine, in the free state, has the same value as in combination; and that sulphur possesses one of its combined values; (3), that this one is the lower of the two.

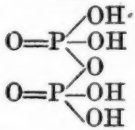
It is therefore necessary to ascribe two atomic volumes to phosphorus, viz., 20·8 in compounds in which it acts as a pentad, and when free, and 25·3 in its triad capacity.

As ortho-phosphoric acid is obtainable directly from the oxychloride by the action of water, there can be no doubt whatever that the formulæ of the phosphoric acids must be represented thus:—

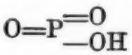
Orthophosphoric acid.



Pyrophosphoric acid.



Metaphosphoric acid.



From the known analogy between vanadium and phosphorus it is highly probable that similar results will follow on investigation.

It remains to mention one conclusion deducible from the facts detailed in the foregoing paper: that as elements enter into combination with a volume which they possess in the free state, the theory of "steres," as applied by Schröder to boiling liquid compounds, is absolutely untenable.

IX.—*On the Specific Volume of Chloral.*

By Laura M. Passavant, Brown Scholar in the Yorkshire College, Leeds.

Among the substances selected by Dr. Thorpe as constituting the experimental groundwork of his investigation "On the Relation between the Molecular Weights of Substances and their Specific

Gravities when in the Liquid State" (*Chem. Soc. J.*, March, *et seq.*, 1880) was chloral. The main point of interest connected with the determination of the specific volume of this body arises from its relation to aldehyde, and from the fact, therefore, that its oxygen-atom would presumably have the same value as in that compound. It was part of Dr. Thorpe's original scheme of work to determine how far the introduction of the three chlorine-atoms in place of hydrogen would modify the specific volume of the compound. Considerable difficulty was met with in procuring this body in a fit state for physical examination, owing to the persistency with which gas-bubbles made their appearance in the liquid when it was heated much beyond 60°. No two samples of chloral could be obtained of identical specific gravity, even although prepared and dehydrated under similar conditions. This circumstance is undoubtedly connected with the tendency of chloral to pass into a polymeric modification, but unfortunately the causes determining this tendency are too incompletely understood to be applied in maintaining this body in a stable condition.

At Dr. Thorpe's suggestion I have again essayed to determine the specific volume of chloral. The greatest care was taken to dehydrate the liquid, and to avoid the formation of free hydrochloric acid, which appears to have a marked influence in polymerising the substance. Although a considerable interval of time has elapsed since the observations which form the subject of the present communication were made, the chloral used has maintained its limpidity unimpaired, and there is no evidence of the formation of metachloral within it.

The liquid was prepared from commercial recrystallised hydrate by treating it with strong oil of vitriol, and afterwards distilling it twice over lime. It was observed that on adding the chloral hydrate to strong sulphuric acid the temperature was reduced by 17°; the temperature of the acid having been 13°, and that of the mixture falling to −4°. The dehydrated chloral was always redistilled before each operation.

In order to verify its purity its vapour-density was determined with the following results. The apparatus employed was the modified Gay-Lussac-Hofmann apparatus described by Dr. Thorpe:—

Weight of liquid	0·1898 gram.
Volume of vapour, corrected for expansion of glass, error of meniscus, &c.	91·74 c.c.
Temperature	99·96°
Barometer (reduced)	758·93 mm.
Mercury column (reduced).....	426·9 „

Found .... 72·21 Calculated .... 73·48

Determination of Boiling Point.—This was effected in the manner

described in the memoir above referred to, and with the same thermometers.

The liquid began to boil at 96°, and that portion was collected separately which came over between 96·8° and 97·3° (uncorr.).

Observed temperature	97·05°
Temperature of the cooled column	23·8°
Length of the cooled column in degrees ..	42
Barometer (reduced).....	747·7 mm.

Corrected and reduced boiling point 97·73°.

Specific Gravity.—The specific gravity was determined upon two samples in separate bottles. The bottles used had graduated stems, and were fitted with ground-glass stoppers. The weighings were made by the method of vibrations, and the weights are reduced to a vacuum. The specific gravities are finally reduced to the temperature of 0°, and compared with water at 4° by means of the tables of expansion given below:—

Bottle 1.

Weight of chloral at div. 40 and 15·4°	8·99126 grams.
Weight of water at div. 40 and at 15·04° ..	5·92866 „
Vol. of water at 15·4°	1·000904
Vol. of water at 15·04	1·000847

Sp. gr. at 15·4° compared with water of same temp. 1·5167

Vol. of chloral at 15·4°	1·017424
Vol. of water at 15·4	1·000904

Bottle 2.

Weight of chloral at div. 35·5 and 15·4° ..	7·83577 grams.
Weight of water at div. 35·5 and 15·4	5·16691 „
Vol. of water at 15·4°	1·000904
Vol. of water at 15·04	1·000847

Sp. gr. at 15·4° compared with water of same temp. 1·5166

Vol. of chloral at 15·4°	1·017424
Vol. of water at 15·4	1·000904

The results of the specific gravity determinations at 0° compared with water at 4° are:—

Determination I	1·54179
Determination II	1·54170

Dr. Thorpe obtained 1·5439 and 1·5466, but was disposed to give the former number double the weight of the latter, as it was made upon a larger quantity of the liquid obtained from a much larger preparation.

Both our numbers differ very widely from that obtained by Kopp, viz., 1·5183.

The determination of the rate of expansion was made in one of the dilatometers employed by Dr. Thorpe; this was filled and heated in the arrangement described in his memoir.

The results are as follows:—

Air-therm. degrees.	Observed vol.	Calculated vol.
0·0	2904·14	2903·997
9·63	2934·19	2934·75
17·57	2960·10	2960·63
26·22	2989·22	2989·43
35·26	3020·60	3020·63
44·30	3052·18	3052·53
52·30	3080·92	3081·54
61·14	3113·93	3114·53
70·12	3149·10	3149·079
78·91	3183·56	3183·98

No observations could be taken beyond 79°, owing to the formation of a bubble of gas in the liquid. These numbers lead to the formula—

$$2903{\cdot}997 + 3{\cdot}155102t + 0{\cdot}0038007t^2 + 0{\cdot}0000149631t^3,$$

which, after dividing through by the first term, and correcting for the expansion of the glass of the dilatometer (0·00002303), gives—

$$V = 1 + 0{\cdot}001109498t + 0{\cdot}0000013338t^2 + 0{\cdot}0000000051827t^3.$$

By means of the formula the volumes of chloral at every 5° between 0° and 100° have been calculated, on the assumption that this expression correctly represents the expansion between these limits:—

°	Volume.	Difference.
0	100000	—
5	100558	558
10	101123	565
15	101696	573
20	102276	580
25	102865	589
30	103463	598
35	104069	606
40	104685	616
45	105310	625
50	105946	636
55	106592	646
60	107249	657
65	107918	669

Δ	Volume.	Difference.
70	108598	680
75	109290	692
80	109995	705
85	110713	718
90	111444	731
95	112188	744
100	112947	759

This formula agrees fairly well with that calculated by Dr. Thorpe from his observations, but is quite different from that of Kopp (*Annalen*, **95**, 307), as will be evident from the following comparison:—

	20°.	40°.	60°.
L. M. P.	10228	10469	10725
Thorpe	10226	10462	10717
Kopp	10187	10385	10615

The relative volume of chloral at its boiling point (97·73A) is 1·12602, as calculated from my observations. Hence its specific gravity at this temperature is $\frac{1{\cdot}54179}{1{\cdot}12602} = 1{\cdot}3692$ compared with water at 4°, and accordingly its specific volume is $\frac{147{\cdot}01}{1{\cdot}3692} = 107{\cdot}37$.

This number agrees almost exactly with that calculated by means of the final values deduced by Dr. Thorpe from his observations, viz., 107·8 (C = 11, Cl = 22·7, H = 5·5, O = 12·2), and shows that the oxygen-atom in chloral has precisely the same value that it has in aldehyde.

X.—*On the Absorption Spectrum of Ozone.*

By W. N. Hartley, F.R.S.E., Professor of Chemistry, Royal College of Science for Ireland, Dublin.

In the year 1878 I made arrangements for investigating the absorption spectrum of ozone, having an idea derived from former experience that it would be less diactinic than oxygen. Several gases were examined at this time, and the general results as to the transparency of carbon dioxide, sulphur dioxide, and hydrochloric acid were similar to those obtained by the late Dr. W. A. Miller. In some experiments more recently made on the diactinic quality of ethylene and acetylene, I have utilised the collimator tube of the spectroscope, which is 36 inches long, by measuring into it the volume of gas to be

observed. The tube, orginally designed for the examination of corrosive gases like ozone, chlorine, and the oxide of nitrogen, was made of glass, and measured 2 feet in length and $1\frac{1}{2}$ in diameter. Near one extremity a side tube of small dimensions was fitted. The ends of the tube were polished and fitted with slices of quartz, luted on with paraffin. The reflections from the inner surface of the glass, which it was at first thought would not affect the photographic plate, led to a want of clearness in the photographs. The apparatus was consequently dismounted for the purpose of blackening the interior of the tube. Being much engaged in the examination of organic substances, I delayed these experiments on ozone, until the announcement of the liquefaction of this remarkable body by Messrs. Hautefeuille and Chappuis (*Compt. rend.*, **91**, 522) attracted my attention once more to the subject.

The following arrangements were made for producing ozone and delivering exactly measured quantities of ozonised oxygen:—A reservoir, containing about 20 cubic feet of oxygen, was connected first with a drying bottle E, 12 inches high, holding about half a litre of oil of vitriol. On the surface of the vitriol a large quantity of pumice crushed into pieces the size of a pea, was placed, and ignited with sulphuric acid previous to use. As the gas bubbles through the vitriol, it keeps the pumice constantly moistened with acid, at the same time that it is itself most thoroughly dried by the large surface of pumice. The gas then passed through a long glass worm-tube D, kept surrounded by ice. One of Tisly and Spiller's ozone tubes C,

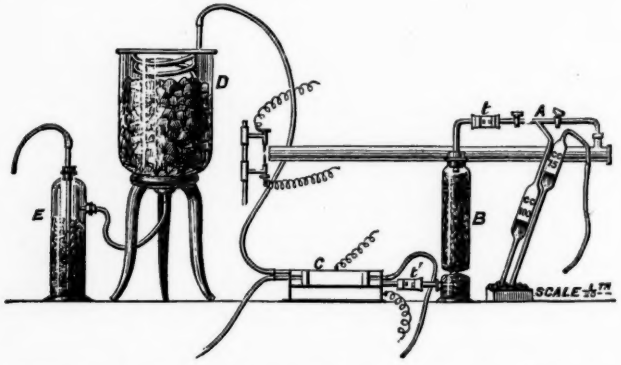


DIAGRAM SHOWING THE APPARATUS FOR DELIVERING MEASURED VOLUMES OF OZONE.

through which a stream of water was kept in circulation, was attached to the worm-tube. The coil and Leyden jar, used as the source of the rays by which the photographs were taken, served likewise to charge

the ozone tube. The ozonised oxygen passed from the tube into a French drying bottle B, 18 inches high, containing pumice soaked in potash solution, containing one part of potash in two of water, and at the top small pieces of stick-potash were placed. This precaution was taken in order to absorb any possible traces of oxide of nitrogen or chlorine. The sticks of potash were subsequently found to be coated with a yellow efflorescence, which proved to be potassium peroxide. Attached to this purifying tube was the apparatus for measuring the purified ozonised oxygen, and delivering it into the collimator tube. This consisted of a **T**-piece A, with two glass stopcocks, joined to a gas-pipette capable of delivering 75 c.c. after each filling. The liquid in the gas-pipette was oil of vitriol. One limb of the **T**-piece was bent downwards at right angles and placed within a tube soldered on at right angles to the collimator tube, the junction between the glass and the metal tubes being luted up with softened paraffin. The other limb of the **T**-piece was fixed on the purifying tube. All joints in the apparatus, subject to the action of ozone, were either of paraffin luting, fused glass, or cork junctions at t and t', the corks being soaked in melted paraffin. On commencing operations, oxygen is blown into the collimator tube through the whole apparatus until it issues abundantly from the slit at the end. A photograph is now taken of the spectrum transmitted by the tube full of oxygen. Then the ozonising tube is charged, and the gas passed into the apparatus for some time, until no more absorption of ozone takes place in the potash-tube. To prevent the gas gaining access to the spectroscope at this stage of the proceedings, the stopcock just beyond the potash purifier is taken out of its setting, in order that the gas may escape here. When the ozone coming off is of a proper strength, it is unbearably strong in smell and exceedingly irritating to the mucous membrane. The stopcock is now replaced and turned so as to be open; that next the collimator tube is left closed. By drawing up the sulphuric acid into the upper bulb of the gas-pipette, the lower one is filled with ozonised oxygen of the same volume as the sulphuric acid withdrawn. By shutting the tap on the supply pipe and opening that communicating with the collimator tube, a measured volume of gas is delivered into it. This operation may be repeated again and again with great rapidity; and as it takes but two or three seconds to take a photograph after each such additional volume of gas, there is no time for loss of oxygen by diffusion, or by oxidising action on the metal tube. About twenty photographs were taken in three or four different series, the various degrees of absorption noticed being due to different quantities of ozone delivered into the collimator tube. The first photograph taken showed a broad absorption-band, stretching from wave-length about 285 to 233 millionths mm. In this case the

collimator tube was filled with ozonised oxygen at a temperature of 16° C., and under a barometric pressure of 774 mm. The contents of the tube were 811·5 c.c. A series of photographs was then taken, the tube being filled first with ozonised oxygen, and this being gradually displaced by successive additions of atmospheric air or oxygen. The increased diactinic character of the gas caused by successive additions of air is well shown in Diagram 2. The tension of the ozone was found by filling stoppered cylinders with the gas and inserting the stoppers. These cylinders were made with funnel-shaped necks, and into the funnel, forming a hydraulic lute to the stopper, a solution of potassic iodide was poured. The stopper being gently loosened, some of the liquid ran into the cylinder without allowing a single bubble of gas to escape; after standing some little time, more of the liquid is allowed to run in; the bubble or two of gas escaping is quite de-ozonised by the potassic iodide solution through which it passes. After the whole of the ozone has been absorbed, starch-paste is added, and the liquid titrated with centinormal solution of sodium thiosulphate.

The potassium iodide was *neutral:* hence two atoms of iodine would represent only one-third of a molecule of ozone.

The actual amount of ozone found in the tube in two separate experiments was—

I .... 0·00048 gram in 493 c.c.
II .... 0·00054 „ „

I .... 0·236 c.c. in 493 c.c. or $\frac{1}{2089}$ of its volume.
II .... 0·260 „ „ or $\frac{1}{1890}$ „

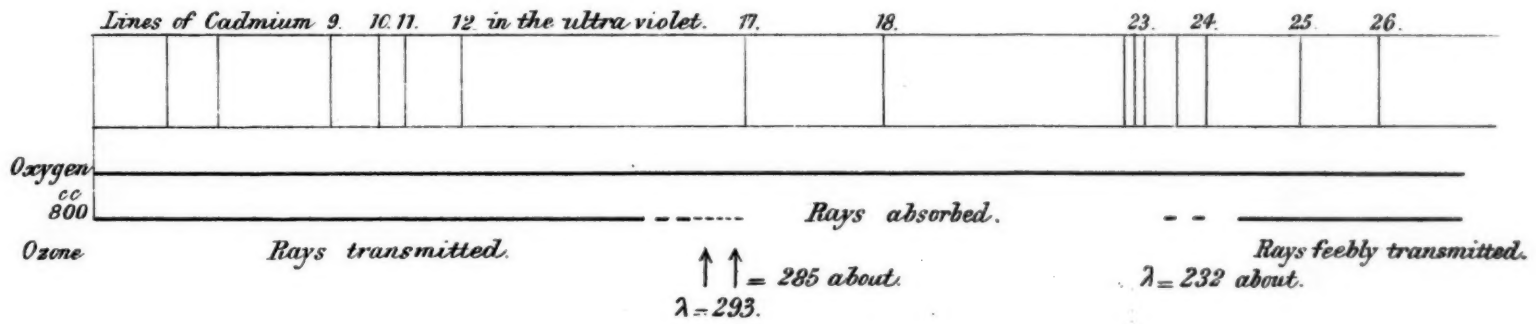
This may be considered as 1 volume of ozone in 2,000 of the oxygen.

The mean wave-length of the rays intercepted by ozone is 256 millionths mm. From this the mean rate of vibration of the molecule of ozone may be calculated. When perfect absorption occurs, the molecule of the absorbing medium must be vibrating synchronously, and in the same plane with the ray absorbed, from which it follows, if the velocity of light be taken as 315,364,000 metres* per second, the mean rate of vibration per second of the molecule of ozone must amount to 1,231,000,000,000,000 vibrations.

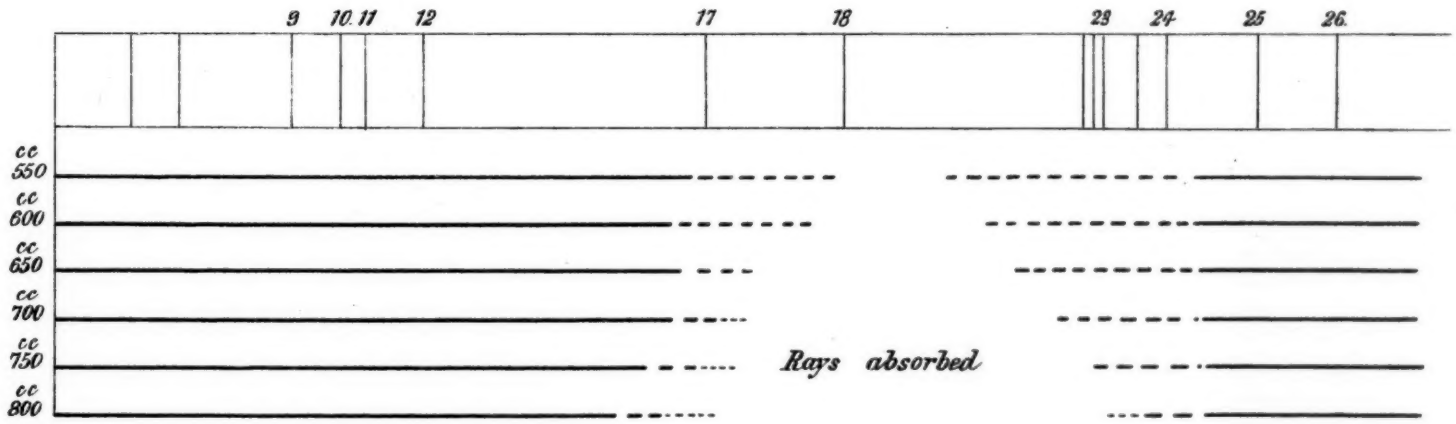
* Fizeau estimated the velocity of light as equal to 78,841 leagues per second, a league measuring four kilometres.

ACTINIC TRANSPARENCY OF OXYGEN COMPARED WITH ITS OPACITY AFTER OZONISATION.

Stratum of gas 36 inches in length. Proportion of $O_3 = \frac{1}{2000}$ vol.



SPECTRA TRANSMITTED BY DIFFERENT QUANTITIES OF OZONISED OXYGEN.



The proportion of ozone in the oxygen was 1/2000ths by volume.

The stratum of gas was 36 inches in thickness.

Here the rays are faintly transmitted. Very faint rays are represented by dotted lines.

Harrison & Sons, Lith. St Martins Lane, W.C.

XI.—*Analyses of Queensland Soils.*

By Professor Liversidge, Assoc. R.S. Mines, F.I.C., &c.

The accompanying analyses of soils from a sugar plantation in Queensland may not, perhaps, be without interest to some, inasmuch as they are from a plantation which was almost exempt from the so-called "disease" or rust, at a time when most of the surrounding plantations had lost a very large proportion of their crops.

The samples were collected with great care, and the top-soil kept distinct from the subsoil.

The analyses were made upon those portions of the air-dried soils which passed through a sieve of 30 holes to the inch, so as to obtain samples of fair average composition, the coarser parts being determined separately; the presence of pebbles, gravel, coarse sand, and large fragments of vegetable fibre would necessarily have caused a great want of uniformity in composition.

In the case of soil No. 3, the results of the analyses are given both with and without the pebbles, gravel, and other similar matters, on account of the presence of a very large proportion of such foreign substances: for had the percentage composition been stated in the ordinary way only, a given weight of the soil would appear to be far richer in certain constituents than is actually the case. In other instances, where the amount of these pebbles was not so large, I have not considered it necessary to state the results in both ways.

The analysis of the soil marked No. 4 will afford an idea of the character of the soil of recently cleared scrub land, *i.e.*, land which had been prepared for cultivation, but had not been cropped.*

The soil marked No. 5 is an example of a poor alluvial soil, which yielded a diseased crop, and No. 6 may be taken as a soil of good quality.

Analyses of Sugar-cane Soils from the Mary River, Queensland.

No. 1. *Surface Soil.*—A rich-looking alluvial soil, of a grey-brown colour when dry, rather lumpy; a fair amount of vegetable fibre present, but easily friable.

Subsoil.—Of a light clay colour, lumpy, but friable; the amount of vegetable fibre present is, as might be expected, considerably less than in the top-soil.

No. 2. *Surface Soil.*—Of the same colour as No. 1 top-soil, but of a rather lighter shade, of fine grain, and but slightly lumpy; the amount of vegetable fibre present is not large.

* "Report upon the Diseases in the Sugar Cane," Queensland, by A. Liversidge. Sydney, 1876.

Analyses of Sugar-cane Soils from the Mary River, Queensland.

	1.		2.		3.				4.	5.	6.
	Surface-soil.	Subsoil.	Surface-soil.	Subsoil.	Surface-soil.		Subsoil.				
Silica and substances insoluble in hydrochloric acid	84·89	78·52	85·39	85·97	84·51	35·435	75·08	39·687	85·30	90·98	82·95
Carbon	1·46	1·05	1·73	0·67	4·45	1·866	0·56	0·296	1·14	1·29	2·01
Nitrogen	0·15	0·09	0·16	0·10	0·21	0·888	0·04	0·021	0·27	0·21	0·19
Soluble silica	0·13	0·09	0·23	0·06	0·08	0·033	0·33	0·174	0·04	0·07	0·04
Alumina	3·82	6·01	3·36	5·39	2·37	0·994	7·65	4·044	3·50	2·24	4·08
Ferric oxide	1·56	4·03	1·41	0·13	0·02	0·009	4·09	2·162	2·55	1·45	3·25
Ferrous oxide	0·76	0·49	0·85	0·63	0·55	0·231	0·29	0·153	—	—	—
Manganous oxide	0·03	traces	0·02	traces	0·02	0·009	—	—	traces	—	traces
Lime	0·43	0·21	0·31	0·18	0·32	0·134	traces	—	0·46	0·36	0·42
Magnesia	0·04	traces	0·04	0·02	0·06	0·025	traces	—	0·01	0·59	0·22
Potash	0·17	0·11	0·15	0·10	0·32	0·134	0·12	0·063	0·12	0·22	0·64
Soda	—	0·24	0·29	—	0·31	0·130	0·09	0·048	0·37	0·03	0·13
Chloride of sodium	0·98	0·04	0·09	0·25	0·11	0·046	0·24	0·127	0·09	0·31	0·06
Phosphoric acid (P_2O_5)	0·09	0·07	0·13	0·03	0·23	0·096	0·02	0·011	0·61	0·09	0·37
Sulphuric acid	0·04	0·02	0·04	0·03	0·03	0·013	0·03	0·016	traces	—	traces
Carbonic acid	0·39	traces	0·22	0·10	0·26	0·109	traces	—	0·22	—	0·02
Moisture expelled at 120° C.	1·93	3·68	1·98	2·55	2·15	0·901	4·41	2·331	1·55	0·71	2·00
Combined moisture	3·13	5·35	3·60	3·79	4·00	1·677	6·79*	3·589*	3·77	1·45	3·62
Undetermined constituents							0·26	0·138			
	100·00	100·00	100·00	100·00	100·00	41·930	100·00	52·860	100·00	100·00	100·00
Associated with the above in the air-dried soil:—											
Sand, gravel, stones, &c.	1·30 per cent.		1·85 p.c.	1·10 p.c.	—	57·66	—	47·140	0·87 p.c.	1·48 p.c.	5·10 p.c.
Woody fibre	0·15 „		0·11 „	0·04 „	—	0·41	—	traces	0·10 „	0·16 „	0·13 „
						100·00					

The sand, gravel, stones, &c., include all those portions of the soil which, after gentle crushing, failed to pass through a sieve of 30 holes to the square inch.

* The combined moisture was in this case determined by heating to redness and collecting the water by means of a chloride of calcium tube. Part of this water was of course derived from the combustion of the diffused organic matter.

Subsoil.—This soil possesses much the same characteristics as No. 1 subsoil. It is, however, a shade lighter, and not quite so lumpy.

No. 3. *Surface Soil.*—Of a rich dark-brown colour, very loose and friable, but much mixed with large jasper and other pebbles; the amount of the vegetable fibre very noticeable.

Subsoil.—A clayey soil, mottled with red; plastic when wet; dried into lumps; contains much gravel; vegetable fibre almost absent.

Soil No. 4.—From new scrub land. A rich brown loamy soil; contains a fair amount of vegetable fibre, and but little sand.

Soil No. 5, which had yielded "diseased" rappoe cane. The air-dried soil was of grey-brown colour, very sandy, and loose, of but poor appearance. A small quantity of vegetable fibre present.

Soil No. 6, which had yielded a healthy crop of rappoe cane. Of brown colour, with yellow shade; dried into rather stiff lumps, with clay-like appearance; contained a small proportion of vegetable fibre. Apparently of fair medium character.

XII.—COMMUNICATIONS FROM THE LABORATORY OF UNIVERSITY COLLEGE, BRISTOL.

On the Volumes of some Compounds of the Benzene, Naphthalene, Anthracene, and Phenanthrene Series.

By W. Ramsay, Ph.D.

(1.) The difference between the observed and the calculated volumes of members of the aromatic series has been long noticed; but, so far as I am aware, never carefully tabulated. The following determinations were made by Kopp, and published in the *Annalen der Chemie*, **96**:—

	Found.	Calculated.	Difference.
Benzene.....	96	99	+ 3·0
Phenol	103·6—104	106·8	2·8—3·2
Benzoic acid.....	126·9	130·8	3·1
Benzoic aldehyde..	118·4	122·2	3·8
Benzyl alcohol....	123·7	128·8	5·1
Methyl benzoate ..	150·3	152·0	1·7
Ethyl benzoate....	174·2	174·0	— 0·2
Amyl benzoate....	247·7	240·0	— 7·7
Ethyl cinnamate...	211·3	218·0	+ 6·7
Methyl salicylate..	157·0	159·8	2·8
Cuminol.....	189·2	183·8	— 5·4
Cymene.....	183·5	187·0	+ 3·5

The numbers assigned by Kopp to hydrogen (5·5), carbon (11·0), and oxygen (7·8 and 12·2), are used in calculating the theoretical molecular volumes of these substances.

It is noticeable that in almost every case the number found is less than that required by theory.

(2.) I have repeated the determination of a number of such compounds, using perfectly pure substances (except in the case of xylene), by the method of which an account is published in the *Journal of the Chemical Society* for 1879, p. 473. In most cases the determinations have every probability of being exact, but with some, especially with phenol, thymol, and benzyl chloride, boiling took place in the bulb, and the specific gravity is less, and consequently the specific volume and the molecular volume greater than they probably should have been. No such difficulty was experienced with the hydrocarbons; the determinations may therefore be accepted as correct. I give measurements first, reserving discussion of results till later.

Substance.	Formula.	b. p.	Mol. vol. found.	Mol. vol. calculated.	Difference.
Benzene.....	C_6H_6	80°	95·80	99	3·20
Toluene.....	C_7H_8	111	118·51	121	2·49
Xylene.....	C_8H_{10}	135—140	136·85	143	6·15
Mesitylene.....	C_9H_{12}	163·5—164	162·19	165	2·81
Cymene.....	$C_{10}H_{14}$	175	181·62	187	5·38
Chlorobenzene	C_6H_5Cl	134·5—135	114·47	116·3	2·83
Phenol.....	C_6H_6O	180	101·17	106·8	5·63
Benzyl chloride ...	C_7H_7Cl	176	133·17	136·3	3·13
Benzoic acid.....	$C_7H_6O_2$	255	126·00	130·0	4·00
Methyl benzoate...	$C_8H_8O_2$	196	149·76	152·0	2·24
Methyl salicylate ..	$C_8H_8O_3$	217	155·90	159·6	3·70
Thymol.....	$C_{10}H_{14}O$	235	189·33	194·8	5·47

(3.) Here it is at once noticeable that the numbers found are in every case smaller than those calculated. Taking the averages of all the differences, we obtain the number 3·92. Omitting xylene, phenol, methyl salicylate, and thymol, of which, for reasons already given, I doubt the accuracy, the mean of the remaining eight differences is 3·26. The mean of the differences of the nine compounds given by Kopp, omitting those which give minus quantities, is 3·54, a number which agrees sufficiently well with that found by me.

(4.) It appears then, that in aromatic compounds, condensation takes place. It is clear that this condensation is independent of the oxygen in the molecule, for it is common to hydrocarbons and to compounds containing oxygen: it cannot be attributed to hydrogen, for the atomic volume of hydrogen probably agrees with that of other

monad elements in being constant. It must, therefore, be dependent on the carbon.

(5.) The molecular volumes of naphthalene and of naphthol have also been determined with the following results:—

	Found.	Calculated.	Difference.
Naphthalene, $C_{10}H_8$....	145·46	154	8·54
Naphthol, $C_{10}H_8O$.....	149·56	161·8	11·24

And similarly, those of anthracene and phenanthrene:—

	Found.	Calculated.	Difference.
Anthracene	195·82	209	13·18
Phenanthrene.....	196·71	209	12·29

The mean of the differences in the former case is 9·89, and in the latter, 12·72.

(6.) I am inclined to attach more reliance to the determination of the volume of naphthalene than to that of naphthol: the results of individual experiments are more in accordance with each other. The numbers are as follows:—

	Specific gravity.	Specific volume.	Molecular volume.
I	0·8799	1·1365	145·47
II	0·8812	1·1348	145·26
III	0·8787	1·1379	145·65
Mean...	0·8799	1·1364	145·46

The results with phenanthrene are also fairly concordant:—

	Specific gravity.	Specific volume.	Molecular volume.
I	0·9066	1·1036	196·34
II	0·9054	1·1044	196·59
III	0·9026	1·1078	197·20
Mean...	0·9048	1·1051	196·71

Very similar results were obtained with anthracene; they serve to show the accuracy of the process, provided boiling in the bulb does not take place.

(7.) Accepting for the meantime that the volumes of molecular proportions of liquids are comparable at their boiling points under a pressure of 760 mm. (an assumption which I propose to discuss at a future time), we see that there is a certain regularity in the differences between theory and practice in the aromatic series, the naphthalene series, and the anthracene series, when compared with one another. If the number 3·92 be accepted as the difference for the aromatic series, we must ascribe it to the condensed formula of benzene, where 6 atoms of carbon have, under ordinary circumstances, only six affini-

ties permitting of combination with other elements or radicles. In naphthalene, 10 atoms of carbon have eight such affinities, and in anthracene and phenanthrene, 14 atoms have ten affinities. It is, I think, a fair assumption to suppose the condensation to be proportional to the total number of atoms of carbon in the compound, and at the same time to the number of affinities of these atoms capable of coming into action. Whether this be the case or not, it is evident that there is a certain proportionality observable in the condensation of members of the benzene, naphthalene, and anthracene series.

XIII.—*On the Atomic Volume of Nitrogen.*

By W. Ramsay, Ph.D.

1. From the preceding paper it is evident that the calculated molecular volumes of members of the aromatic series are in excess of the real volumes by a number which may be accepted as approximately 3·5. As the value of the element nitrogen has been calculated chiefly from data furnished by aromatic compounds, it is necessary to apply a correction. It must, I think, be allowed that the atomic volumes of elements as first adopted by Kopp, were accepted as merely a fair approximation to the correct values. I hope on a future occasion to consider those of carbon, hydrogen, and oxygen, but I take this opportunity of pointing out on what very slender grounds the commonly accepted value of nitrogen in amines, viz., 2·3, is received.

2. The only liquid containing nitrogen, of which Kopp carefully determined the expansion, was an aromatic one—aniline. Its volume at the boiling point, on the basis of molecular weight, was found to be 106·4—106·8. From the values for carbon and hydrogen, deduced from observations on members of the fatty series, the value of C_6H_7 was calculated to be:—

$$11 \times 6 + 5{\cdot}5 \times 7 = 104{\cdot}5, \text{ and } 106{\cdot}8 - 104{\cdot}5 = 2{\cdot}3.$$

Kopp then assumed that all liquids similarly constituted to aniline have the same coefficient of expansion, and deduced the following table:—

Substance.	Formula.	Observed.	At	By	Calculated.	Difference.
Ammonia	NH_3	22·4 and 23·3	10° and 5·5°	Faraday	18 8	+3·6
Ethylamine	$C_2H_5NH_2$	65·3	8	Wurtz	62·8	+2·5
Amylamine	$C_5H_{11}NH_2$	125·0	18	Wurtz	128·8	−3·8
Caprylamine	$C_8H_{17}NH_2$	190·0	?	Squire	194·8	−4·8
Aniline	$C_6H_5NH_2$	106·4—106·8	near 184°	Kopp	106·8	—
Ethylaniline	$C_6H_5NHC_2H_5$	150·6	18	Hofmann	150·8	−0·2
Diethylaniline ...	$C_6H_5N(C_2H_5)_2$	190·5	18	Hofmann	194·8	−4·3

3. It is noticeable that ethylaniline is the only member of this group of which the observed and calculated volumes are approximately the same, and it (and diethylaniline) are the only two of which this is to be expected, for their rates of expansion may be fairly assumed not to differ much from that of aniline, and they are both aromatic compounds, possessing, as such, "condensed" volumes. Of the others, ethylamine is the only one of which the specific gravity was ascertained not far from its boiling point (18·7°), and its observed volume exceeds its calculated volume by 2·5 units.

4. In 1879 I communicated to the Chemical Society the results of a number of determinations of the molecular volumes of compounds containing nitrogen, of which I reproduce the following:—

	Molecular volume.
Aniline, $C_6H_5NH_2$	109·1
Toluidine, $C_7H_7NH_2$	128·9
Dimethylaniline, $C_8H_9NH_2$	152·4

From the data connected with the molecular volumes of aromatic compounds, adduced in the preceding communication, it is evident that a number differing not greatly from 3·5, must be subtracted from each found volume for each group of C_6H_5 present; for that is the approximate condensation which carbon and hydrogen undergo in forming the phenyl group. Applying this principle, we have:—

Aniline, $C_6H_7 = (6 \times 11) + (7 \times 5{\cdot}5) - 3{\cdot}5 = 101{\cdot}0.$

$109{\cdot}1 - 101 =$ value of $N = 8{\cdot}1.$

Toluidine, $C_7H_9 = (7 \times 11) + (9 \times 5{\cdot}5) - 3{\cdot}5 = 123{\cdot}0.$

$128{\cdot}9 - 123 =$ value of $N = 5{\cdot}9.$

Dimethylaniline, $C_8H_{11} = (8 \times 11) = (11 \times 5{\cdot}5) - 3{\cdot}5 = 145{\cdot}0.$

$152{\cdot}4 - 145 =$ value of $N = 7{\cdot}4.$

The average of these three values is nearly 7.

5. Applying this value to the substances deduced by Kopp, quoted in § 2, and to those directly determined by myself, we have:—

	Found.	Calculated.	Difference.
Ammonia*	22·4	23·5	+ 1·1
Ethylamine*	65·3	67·7	+ 2·4
Aniline.....	109·1	108·0	− 1·1
Toluidine.....	128·9	130·0	+ 1·1
Ethylaniline*	150·6	152·0	+ 1·4
Dimethylaniline	152·4	152·0	− 0·4
Diethylaniline*	190·5	196·0	+ 5·5

* Those substances to which an asterisk is affixed are calculated on the supposition that their expansion is similar to that of aniline.

The agreement between the numbers found and calculated is, I think, sufficient to render the theory on which these calculations are based at least extremely probable; but it is also very strongly supported by an argument furnished by a remark of Kopp's. It may now be accepted as proved that the atomic volume of an element or the molecular volume of a group capable of isolation in the free state is, if not absolutely, at least nearly, identical with the volume which it occupies in compounds.

Now as the product of specific volume and atomic weight is the atomic volume, the specific gravity is deducible from the atomic volume by dividing the atomic weight by the atomic volume. Then, to ascertain the specific gravity of nitrogen at its boiling point—

$$\frac{\text{Atomic weight}}{\text{Atomic volume}} = \frac{14}{2{\cdot}3} = 6{\cdot}1.$$

If the atomic volume of nitrogen in its compounds be 2·3, and if, as has been shown by Mr. Masson and myself to be the case with phosphorus, an element which possesses two separate volumes in compounds in which it has different atomicity, exists in the free state in its more condensed form, then nitrogen at its boiling point is 6·1 times heavier than water at 4°! But if 7 be accepted as the atomic volume of nitrogen, then

$$\frac{\text{Atomic weight}}{\text{Atomic volume}} = \frac{14}{7} = 2,$$

a much more probable result.

It merely remains to be noticed that the number 7 does not greatly differ from that observed in compounds of the pyridine series; and that if the value of O_2 in NO_2 be taken as 24·4, that of nitrogen is equal to 8·6.

XIV.—*On Pentathionic Acid.*

By Vivian Lewes, Assistant in the Laboratories, Royal Naval College.

In March last, at the suggestion of Dr. Debus, I undertook an investigation on the subject of pentathionic acid, the existence of which had been denied.

The analysis of the liquid obtained by the passage of sulphuretted hydrogen and sulphurous acid into water, and the removal of the precipitated sulphur by filtration, by Wackenroder, Kessler, Stingl and Morawski, and quite recently by Takamatsu and Smith, is based on

the assumption that only one acid is contained in the solution; but as this assumption has never been proved, and as we have good reasons for believing that more than one acid is present in the Wackenroder solution, it follows that the existence or non-existence of pentathionic acid cannot be ascertained by a determination of the relative quantities of sulphur and oxygen in combination in this or any liquid of a similar nature.

If only two acids, one of the formula ($H_2S_4O_6$), and the other ($H_2S_6O_6$), 1 molecule of each be present, the analysis of the liquid as conducted by Wackenroder, Kessler, Stingl and Morawski, and Takamatsu and Smith, must give numbers corresponding to the formula ($H_2S_5O_6$), and this result would not establish the existence of pentathionic acid.

No salt of pentathionic acid has hitherto been prepared in a pure state. Lenoir's barium pentathionate contains alcohol, according to him, mechanically mixed with the salt; according to others in chemical combination. Kessler's potassium salt was tetrathionate, and his, as well as Ludwig's barium salt ($Ba_2S_9O_{12}.7H_2O$), which Kessler regards as a double salt of tetra- and penta-thionic acid, may be the salt of an acid ($H_4S_9O_{12}$).

The potassium salt of which Rammelsberg has given a crystallographic description, was probably tetrathionate.

Messrs. Takamatsu and Smith's synthesis of pentathionic acid does not prove the existence of the pentathionate. They decompose plumbic hyposulphite with a concentrated iodine solution, and obtain in this manner what they suppose to be pentathionic acid with lead in solution. The lead is precipitated by means of sulphuretted hydrogen, and after removal of the excess of sulphuretted hydrogen, they obtain a liquid which has the properties of pentathionic acid.

Kessler says, in his paper published in *Pogg. Ann.*, **74**, in 1848, whilst describing the preparation of tetrathionic acid, that the lead salt of this acid must not be decomposed by sulphuretted hydrogen, because the plumbic sulphide has the property of decomposing tetrathionic acid with evolution of sulphurous acid, and the sulphurous acid and sulphuretted hydrogen produce pentathionic acid.

The liquid prepared by Messrs. Takamatsu and Smith probably contains tetrathionic acid or its lead salt, and, if so, their "synthesis of pentathionic acid" would be the preparation of a Wackenroder solution from the old materials (sulphurous acid and sulphuretted hydrogen) developed under the conditions described by Kessler 32 years ago. Accordingly it follows that the existence of the class of bodies called pentathionates has yet to be proved, and to do this, it seemed to me to be absolutely necessary that a pure salt of the acid

should be obtained. This I have succeeded in doing, and now bring my results before the Society.

A solution was prepared by Wackenroder's method of passing continuous streams of sulphuretted hydrogen and sulphurous acid through distilled water, the sulphuretted hydrogen being kept slightly in excess. The gases were well washed, and passed simultaneously into the water through a double delivery tube, so arranged that the gases did not come in contact until in presence of the water, while any gas not decomposed, or dissolved, escaped through a small dip tube, the mouth of which was closed by mercury. A slow continuous stream of the two gases was kept passing through distilled water for about seven hours, at the end of which time a thick magma of sulphur had collected at the bottom of the flask in which the operation was conducted, the liquid itself being full of suspended sulphur.

The liquid was then decanted into a large evaporating basin, and heated for several hours on a water-bath. When the solution had evaporated down to one-fourth of its original bulk the sulphur began to coagulate, and it became possible to obtain a clear liquid by filtration.

The acid liquid so obtained slowly deposited sulphur; this was filtered off, and the total sulphur in the clear acid determined by three distinct processes.

I. By evaporation to dryness with potassic hydrate, and oxidation of the sulphur into hydric sulphate by fusion with potassic hydrate and potassic nitrate, and estimation as baric sulphate.

10 c.c. of the acid solution gave 1·6725 grams of baric sulphate, equal to 0·23 gram of sulphur.

II. By addition of excess of potassic hydrate and oxidation of the sulphur by chlorine gas, and estimation as baric sulphate.

10 c.c. of the acid solution gave 1·656 grams of baric sulphate, equal to 0·227 gram of sulphur.

III. By boiling with mercuric cyanide, and estimation of the hydric sulphate, mercuric sulphide and free sulphur, according to Kessler's equation,

$$H_2S_5O_6 + 2(H_2O) + Hg(CN)_2 = 2(H_2SO_4) + HgS + S_2 + 2(HCN).$$

10 c.c. of the acid solution gave—

Sulphur as hydric sulphate	=	0·096 gram.
„ as mercuric sulphide	=	0·042 „
„ as free sulphur	=	0·088 „
Total	=	0·226

These three distinct determinations of the total sulphur in the Wackenroder acid thus give—

$$\text{Sulphur..} \left\{ \begin{array}{ll} \text{I.....} & 0{\cdot}23 \\ \text{II.....} & 0{\cdot}227 \\ \text{III.....} & 0{\cdot}226 \end{array} \right\} \text{in 10 c.c.}$$

I then determined the capacity of saturation of the solution.

5 c.c. of the acid were taken, and titrated with a standard potash solution, and were found to be able to neutralise 0·0728 gram of potassic oxide.

Thus 1 c.c. of the acid solution will neutralise 0·01457 gram potassic oxide, equal to 0·012 gram of potassium, and the total sulphur in 1 c.c. of the solution is 0·0226 gram.

If these two numbers be respectively divided by the atomic weights of the elements they refer to, we obtain two quotients, standing to each other in the ratio of 2 to 4·55.

This result points to the fact that the acid solution contains a sulphur acid or acids, containing a larger proportion of sulphur than the tetrathionate, and which may be the pentathionate.

On addition of excess of an alkaline hydrate to this solution, a separation of sulphur takes place, with destruction of the higher thionates, but I had many times noticed that when a small quantity of a dilute alkali was slowly added to the acid solution, an opalescence ensued, but no great separation of sulphur took place until the point of neutralisation was approached. This suggested that if a solution of the acid were only partly neutralised with a very dilute solution of an alkaline hydrate, it might be possible to crystallise from the acid solution the salt required.

A Wackenroder solution was taken, concentrated, and freed from suspended sulphur, and its capacity for saturation having been determined, a weak solution of baric hydrate, in quantity sufficient to one-half neutralise it, was added. This produced an immediate precipitate of baric sulphate, together with a slight separation of sulphur. On allowing to stand till the next day and then filtering, a clear solution was obtained; this was placed over hydric sulphate in a vacuum, and left to crystallise. After standing for a few days some sulphur separated; this was got rid of by filtration, and the solution replaced in the vacuum, and at the end of eighteen days it deposited a crop of fine needle-shaped crystals, together with a small quantity of sulphur.

These crystals were drawn and purified by recrystallisation, dried over hydric sulphate and analysed as follows:—A known weight of the salt was taken and oxidised by fuming hydric nitrate, all the sulphur present being converted into hydric sulphate, some of which instantly combines with the barium present, forming baric sulphate,

and this after being freed from all traces of nitrates, gives the whole of the barium of the salt and part of the sulphur.

The hydric sulphate remaining in the filtrate is then estimated by adding baric chloride, and the baric sulphate having been boiled with hydric chloride after ignition as a final precaution, gives the remainder of the sulphur.

0·2215 gram of the salt gave on oxidation 0·124 gram of baric sulphate,

equal to 0·0729 gram of barium or 32·8 per cent.

and equal to 0·01702 gram of sulphur.

The hydric sulphate remaining in solution gave 0·38 gram of baric sulphate = 0·05217 gram of sulphur,

$$\therefore \text{ total sulphur} = 0{\cdot}05217 + 0{\cdot}01702 \text{ or } 31{\cdot}2 \text{ per cent.}$$

A second analysis gave 33·2 per cent. barium,
and 30·1 „ sulphur.

These results agree with the percentage composition of baric tetrathionate with three molecules of water of crystallisation.

		Found.	
Calculated for $BaS_4O_6 3H_2O$.		I.	II.
Barium	33·0	32·8	33·2
Sulphur	30·8	31·2	30·1

This salt crystallises in fine needle-shaped crystals, readily soluble in cold water, not decomposing on boiling.

On addition of strong potassic hydrate to a solution of this salt, it is decomposed, with precipitation of baric sulphite and formation of hyposulphites, but no liberation of sulphur.

After standing for a few days, the mother-liquor gave a second crop of crystals, consisting chiefly of thin square plates mixed with a few small oblong rectangular crystals, which on analysis give results intermediate between the tetra- and penta-thionate, and which are probably a double salt of the two acids.

The mother-liquor on again standing yielded a third crop, consisting of very small oblong rectangular crystals; these were drawn and dried over hydric sulphate, and having been examined under a microscope, were seen to be homogeneous and free from sulphur. They were then finely powdered in an agate mortar and analysed by oxidation of the sulphur with strong fuming hydric nitrate, all the precautions described in the analysis of the tetrathionate being observed.

The water of crystallisation was determined by combustion with plumbic chromate.

I. 0·3835 gram of the salt gave on oxidation 0·2 gram of baric sulphate,

equal to 0·11760 gram barium = 30·6 per cent.,
equal to 0·02746 gram sulphur.

Hydric sulphate remaining in solution gave as baric sulphate 0·798 gram,

equal to 0·10956 gram of sulphur.

Total sulphur = 0·10956 + 0·02746 = 35·78 per cent.

0·1615 gram of the salt on combustion with plumbic chromate gave 0·0205 gram of water = 12·6 per cent.

II. 0·287 gram of the salt gave on oxidation 0·151 gram of baric sulphate,

equal to 0·088788 gram of barium = 30·9 per cent.,
equal to 0·02073 gram of sulphur.

Hydric sulphate remaining in solution gave 0·5955 gram of baric sulphate,

equal to 0·08176 gram of sulphur.

Total sulphur = 0·08176 + 0·02073 = 35·7 per cent.

These results agree closely with the calculated percentage composition of baric pentathionate with three molecules of water of crystallisation.

		Found.	
Calculated for ($BaS_5O_6.3H_2O$).		I.	II.
Barium	30·6	30·6	30·9
Sulphur	35·7	35·78	35·7
Water	12·0	12·6	—

This salt crystallises in small oblong rectangular plates, which in most cases have one corner truncated. This truncation seems to vary considerably, in some cases being very distinct, while in others it is absent.

I have also obtained, by similar means, a baric pentathionate containing more water of crystallisation, and crystallising in rectangular prisms. A full description of this salt, as well as of the intermediate salt, I hope soon to bring before this Society.

The baric pentathionate decomposes when dry at a little below 100° C., yielding baric sulphate, sulphurous acid, sulphur, and water vapour:—

$$BaS_5O_6.3H_2O = BaSO_4 + SO_2 + S_3 + 3H_2O.$$

I attempted to utilise this reaction in analysing the salt, but found it impossible to get off all the water and sulphurous acid at a temperature at which none of the sulphur volatilised.

The salt readily dissolves in cold water, and may be even boiled provided the solution be not too concentrated.

Strong potassic hydrate added to a solution of the salt decomposes it with precipitation of baric sulphite, formation of hyposulphites, and liberation of sulphur.

The remaining reactions of baric pentathionate are the same as those of the acid salt, viz. :—

Argentic nitrate gives a yellow precipitate, darkening on standing, and gradually becoming black.

Ammoniacal argentic nitrate, a violet-brown coloration, blackening on heating or standing.

Mercurous nitrate, a lemon-yellow precipitate, turning white to whitish-grey on standing with excess of the reagent.

Mercuric chloride, a white precipitate sometimes acquiring a slightly yellow tint on standing.

The mother-liquor which gave the three crops of crystals described, deposited a few more crystals of pentathionate mixed with sulphur, and then began to rapidly decompose, giving off sulphurous acid and depositing sulphur.

Having obtained a well defined barium salt, the analysis of which left no doubt as to its composition, I turned my attention to the combinations of the acid with potassium.

A Wackenroder solution was taken and prepared as in the previous case, and having determined its capacity of saturation, dilute potassic hydrate was added in quantity sufficient to half neutralise it. In doing this care was taken to use a very dilute solution of the alkali, and only to add a few drops at a time, stirring well after each addition so as to avoid as much as possible any great separation of sulphur.

The half-neutralised solution was then allowed to stand for 24 hours and was then filtered from a slight precipitate of sulphur that had formed in the liquid, and the filtrate was placed over H_2SO_4 in a vacuum.

At the end of three weeks this solution gave a crop of well-developed monoclinic crystals. These were drawn, rinsed with distilled water, dried over hydric sulphate and analysed, giving results agreeing with the formula for anhydrous potassic tetrathionate.

		Found.	
Calculated for $K_2S_4O_6$		I.	II.
Potassium	25·8	25·6	25·9
Sulphur	42·3	41·2	42·5

This salt crystallises in very fine monoclinic crystals, showing a pair of well-developed pyramid faces, large macro- and brachy-pinacoids, and a small pair of prism faces.

It is readily soluble in water, and the solution gives no precipitate of sulphur on addition of potassic hydrate.

The mother-liquor which gave this first crop, after standing for a few days, gave a second crop of crystals, the bulk of which were evidently the tetrathionate, but mixed with them were some semi-opaque crystals, probably rhombic.

These semi-opaque crystals were picked out and analysed, giving results which showed the salt to be potassic pentathionate with two molecules of water of crystallisation.

		Found.	
Calculated for $K_2S_5O_6.2(H_2O)$.		I.	II.
Potassium	21·08	21·0	21·18
Sulphur	43·2	42·7	43·9
Water.....	9·4	8·2	—

On again standing the mother-liquor deposited a third crop of small and very brilliant crystals.

These were drawn, rinsed with distilled water, dried over hydric sulphate, and analysed, the sulphur being determined as baric sulphate after oxidation with hydric nitrate and precipitation with baric chloride, the precautions described in the analysis of the barium salt being observed; the potassium was determined as potassic sulphate and the water by combustion with plumbic chromate. The results obtained all pointed to the salt being potassic pentathionate with 1 molecule of water of crystallisation.

0·104 gram of the salt gave 0·052 gram of potassic sulphate, equal to patassium 22·4 per cent.

0·502 gram of the salt gave 1·658 gram of baric sulphate, equal to 45·3 per cent. of sulphur.

0·1838 gram of the salt gave 0·0115 gram of moisture, equal to 6·2 per cent. of moisture.

A second analysis gave 22·1 per cent. of potassium.
" " " 44·3 per cent. of sulphur.

		Found.	
Calculated for $K_2S_5O_6.H_2O$.		I.	II.
Potassium	22·1	22·4	22·1
Sulphur	45·4	45·3	44·3
Water	5·1	6·2	—

This salt crystallises in very small and apparently monoclinic crystals not unlike the tetrathionate, but with rather more complicated faces.

After depositing this crop of pentathionate the mother-liquor

rapidly decomposed, giving off sulphurous acid and finally depositing sulphur.

I have obtained by similar means a salt crystallising in very small, short prisms, and which on analysis seems to be anhydrous potassic pentathionate.

	Calculated for $K_2S_5O_6$.	Found.
Potassium	23·3	23·2
Sulphur.....	47·9	47·0

These crystals are often to be found mixed with the crops of small crystals of $K_2S_5O_6.H_2O$.

From this it appears that the potassic pentathionate crystallises in three distinct forms, dependent on the amount of water of crystallisation present.

In making the salts by the method described some of the potassic tetrathionate crystallises out first, then a crop of tetrathionate, mixed with semi-opaque rhombic crystals of the $K_2S_5O_6.2H_2O$, and finally a crop either of the $K_2S_5O_6.H_2O$, or the anhydrous salt or the two mixed, is deposited.

These salts in a dry condition decompose at a little under 100° C., giving off sulphurous acid and leaving potassic sulphate and sulphur.

They readily dissolve in cold water and do not decompose even on boiling, provided the solution be not too concentrated.

Like the baric pentathionate, these salts cannot be recrystallised from an aqueous solution, as on reaching a certain point of concentration they break up into tetrathionate and deposit sulphur.

The potassic pentathionates in solution give an immediate precipitate of sulphur on addition of potassic or sodic hydrate, and this distinguishes these salts from the tetrathionate. Their other reactions are similar to those of the baric pentathionate.

The potassium salts of pentathionic acid are much more stable than the barium salt and can be easily prepared, the mother-liquor not being so apt to decompose and deposit sulphur.

A more convenient method of making the salts is to prepare a Wackenroder solution and to one-half neutralise it, without coagulating the sulphur by evaporation. The partial neutralisation causes the sulphur to settle out in the plastic condition, the clear solution can be then evaporated in a vacuum over hydric sulphate.

In preparing the Wackenroder solution the sulphurous acid is best kept slightly in excess, as, although this causes a larger formation of tetrathionate, it also seems to prevent the decomposition of the mother-liquor and the precipitation of sulphur.

I am now working upon some other salts of the higher thionates, and hope before long to bring the results of my experiments before this Society.

XV.—CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF TÔKIÔ, JAPAN.

No. IV. *On Menthol or Peppermint Camphor.**

By M. Moriya, Graduate in Chemistry in the University of Tôkiô.

Samples of peppermint camphor were obtained from various parts of Japan. One, from the province of Bichû, consisting of large snow-white crystals, was found to contain 10·25 per cent. of hydrous magnesium sulphate. That used for the experiments was from Youezana, and free from adulteration; it was recrystallised from oil of peppermint several times. The mean melting point of this sample was 37·2°, its solidifying point 35°. Another sample separated from crude peppermint oil by means of a refrigerating mixture, fused at 35°, but on repeatedly pressing the crystals between blotting paper, the melting point rose to 39°.

Menthol has the specific gravity 0·890 at 15° compared with water at 15°. It distils unchanged at 210—212°. Its (apparent) specific rotatory power in alcoholic solution (strength of alcohol not stated) as determined with a Soleil-Ventzke saccharimeter for two solutions containing 10·673 and 8·363 grams respectively in 100 c.c. at 15° is $[\alpha]_j = -59·3°$.

On heating with potassium dichromate and sulphuric acid in sealed tubes at 120° for about ten hours, it furnished as sole product an oil boiling at 204—205°, which on analysis gave numbers agreeing well with the formula $C_{10}H_{18}O$. The same substance was obtained, together with the acetate described by Oppenheim, on similarly heating a solution of menthol in glacial acetic acid with the dichromate mixture. The oil in question has the specific gravity 0·9032 at 15°, and is readily soluble in alcohol, ether, and chloroform, but insoluble in water; it has an agreeable fragrant odour, is optically inactive, and does not solidify when cooled by ice and salt.

Action of Nitric Acid upon Menthol.

When menthol is warmed with about five times its volume of fuming nitric acid, a violent reaction sets in, and a large amount of nitrous fume is evolved, whilst a yellowish-green oil is produced. It was separated from the acid liquid, washed with water, and dried over

* Being the substance of a thesis presented on graduating, July, 1880. The first part of the essay consisted of a description of the manufacture of peppermint camphor.—R. W. A.

calcium chloride. It is an explosive body, readily decomposing on the application of heat, with liberation of nitrous fumes. It is insoluble in water, but dissolves easily in alcohol and ether. Its specific gravity at 15° C. compared with water at the same temperature is 1·061. On account of its explosive character, its composition was not determined.

When this nitro-compound was treated with zinc and dilute sulphuric acid, a reddish-brown thick oil was formed, which after separating from the acid liquid, was dried over calcium chloride. On distillation, a small quantity of water and a colourless oil passed over below 120°, after which the temperature rose rapidly to 185° to 190°, when a clear yellow oil distilled, and a black resinous matter was left which, on cooling, solidified to a hard, black mass. The yellow oil on combustion gave the following numbers. The nitrogen was determined by Dumas' method.

1. 0·2177 gram gave 0·6152 gram CO_2, and 0·2596 gram H_2O.
2. 0·2015 „ 0·5715 „ 0·2451 „
3. 0·4305 „ 35·5 c.c. N at 17° and 768·3 mm. barometric pressure.
4. 0·3641 gram gave 31·5 c.c. N at 18° and 765 mm. barometric pressure.

	1.	2.	3.	4.	Mean.	Calculated for $C_{10}H_{19}NH_2$.
Carbon....	77·07	77·33	—	—	77·20	77·42
Hydrogen .	13·25	13·51	—	—	13·38	13·55
Nitrogen..	—	—	9·62	10·02	9·82	9·03
					100·40	100·00

These numbers agree sufficiently well with the formula $C_{10}H_{19}.NH_2$, and they suggest that the nitro-compound has the formula $C_{10}H_{19}.NO_2$.

The amido-compound has a peculiar odour, and its yellow colour changes to bright red on exposure to air for some time. It is soluble in alcohol and ether, but insoluble in water. It has no action on polarised light.

A dark heavy oil was obtained by the action of hydrochloric acid upon the amido-compound, but its amount was too small to permit of its being purified for analysis.

When menthol was heated for a long time with about 20 times its volume of fuming nitric acid, it dissolved completely, and a deep yellow liquid was obtained which was evaporated on the water-bath to a small bulk, and then left for two days. Clusters of a fine white crystalline substance were found in the liquid, and were dried by pressure between blotting paper. They dissolved completely in both water and alcohol, and were purified by recrystallisation from water,

and drying between blotting paper. On combustion they yielded the following numbers :—

1. 0·2746 gram gave 0·4208 gram CO_2 and 0·1685 gram H_2O.
2. 0·2350 „ 0·3624 „ 0·1428 „

	1.	2.	Mean.	Calculated for $(C_5H_8O_4)_2H_2O$.	Calculated for $C_5H_8O_4$.
Carbon.....	41·80	42·05	41·92	42·55	45·45
Hydrogen	6·81	6·80	6·805	6·39	6·06
Oxygen	—	—	51·275	51·06	48·49
			100·000	100·00	100·00

No nitrogen was found in the crystals.

The crystals dissolve readily in water and alcohol, and have a faint peculiar odour. They melt, after long drying between filtering paper, at 96·5°. Their aqueous solution gives a white precipitate with baryta-water. The precipitate was collected, washed, and dried at 100°. It was then heated with hydric sulphate, and ignited, and gave the following result :—

1. 0·4946 gram gave 0·4225 gram $BaSO_4$.
2. 0·6076 „ 0·5205 „

	1.	2.	Mean.	Calculated for $(C_5H_6BaO_4)_2H_2O$.	Calculated for $C_5H_6BaO_4$.
Barium ...	50·25	50·39	50·32	49·63	51·30

The aqueous solution also gives a white precipitate with silver nitrate and with calcium chloride. A quantity of the crystals was dissolved in water and fractionally precipitated with silver nitrate. The precipitates after being dried at 100° were decomposed with hydric nitrate, and the silver determined as chloride.

1. 0·3143 gram of the first precipitate gave 0·2798 gram AgCl.
2. 0·4336 „ second „ 0·3541 „
3. 0·2507 „ third „ 0·2052 „
4. 0·3085 „ fourth „ 0·2514 „

	Silver. Per cent.	Calculated for $C_5H_6Ag_2O_4$. Per cent.	Calculated for $C_5H_6Ag_2O_4,\frac{1}{4}H_2O$. Per cent.
1st precipitate	61·70	62·4	60·84
2nd „	61·46		
3rd „	61·60		
4th „	61·33		

The composition of the different precipitates does not differ enough to suggest that the substance was not homogeneous, but the mean number, 61·52 per cent., differs from either of the two calculated per-

centages given. The substance probably corresponded to $C_5H_6Ag_2O_4$ with a small amount of water present as moisture. The evidence leads to the supposition that the acid is normal pyrotartaric acid, $CH_2<\begin{matrix}CH_2.COOH\\CH_2.COOH\end{matrix}$, which melts at 97°. It must be noted, however, that it differs from the acid described by Markownikoff (*Annalen*, **182**, 347—358), in giving precipitates with barium and calcium salts.*

Action of Bromine upon Menthol.

When bromine is added drop by drop to a solution of peppermint camphor in chloroform, reaction takes place very readily, hydrobromic acid being liberated and a reddish-yellow solution being formed. On allowing this solution to stand for several days exposed to light, the colour changes to dark green. An attempt was made to separate the chloroform by distillation, but on heating in a retort to 50° decomposition ensued, large quantities of hydrobromic acid were evolved, and a dark-purplish oil was left in the retort.

The next experiment was slightly modified. A quantity of menthol was dissolved in glacial acetic acid, and to this solution bromine was added drop by drop, a reddish-yellow oil being finally formed. This was separated, washed with water containing ammonia, and finally with pure water, and dried in a vacuum. The amount of bromine was determined by igniting with pure lime in a combustion-tube, dissolving the lime in nitric acid, and, after filtering, precipitating the bromine by silver nitrate:—

1. 0·6344 gram gave 0·5366 gram AgBr.
2. 0·4213 „ 0·3592 „
3. 0·5313 „ 0·4509 „

	1.	2.	3	Mean.	Calculated for $C_{10}H_{19}Br$.
Bromine.....	35·99	36·28	36·12	36·13	36·53

This leads to the formula $C_{10}H_{19}Br$.

The bromo-compound is a clear yellow oil with a peculiar odour; it dissolves freely in alcohol, but is insoluble in water. It is heavier than water. It is very unstable, decomposing when heated, evolving gases, and leaving a carbonaceous mass. It is decomposed by potash.

Experiments were made to obtain a potassium or sodium compound

* The preparation of this substance requires long heating with excess of fuming nitric acid, as the nitro-menthol first formed is oxidised with great difficulty. Intermediate products appear to be formed, as on one occasion the aqueous solution separated from the undecomposed nitro-menthol gave a precipitate with silver nitrate, which on drying and heating suddenly exploded.—R. W. A.

of menthol, but without success. A violent reaction occurred when pieces of sodium were added to fused menthol, but the product appeared to be decomposed when treated with water.

Action of Dehydrating Agents on Menthol.

The hydrocarbon menthene was obtained by Walter by the action of anhydrous phosphoric acid upon peppermint camphor. Oppenheim recommended as the most advantageous method of preparing it to act upon the camphor with zinc chloride. I used the latter method. Menthol was heated with about its own weight of zinc chloride in a retort. The distillate was separated from the water and cohobated with fresh zinc chloride. The product distilled over between 162° and 167°. Oppenheim gives 163° as the boiling point. Combustion gave the following numbers:—

1. 0·1861 gram gave 0·5912 gram CO_2 and 0·2228 gram H_2O.
2. 0·2250 „ 0·7152 „ 0·2720 „

	1.	2.	Mean.	Calculated for $C_{10}H_{18}$.
Carbon	86·64	86·70	86·67	86·96
Hydrogen ..	13·29	13·42	13·36	13·04

It is a colourless, transparent liquid, with an agreeable odour and refreshing taste. It is insoluble in water, but easily soluble in alcohol and ether. Its specific gravity at 15° is 0·814. It is optically inactive. It burns with a bright, smoky flame. Bromine combines with it very readily, forming a dark oil, which is very unstable.

When menthene is heated with a large volume of fuming nitric acid a violent reaction occurs, nitrous fumes being evolved, and the solution on evaporation deposits crystalline clusters. After purification these were found to yield on analysis numbers the same as given by the crystalline substance formed from menthol:—

1. 0·2690 gram gave 0·4117 gram CO_2 and 0·1622 gram H_2O.
2. 0·2181 „ 0·3352 „ 0·1332 „

	1.	2.	Mean.	Calculated for $C_{10}H_{18}O_9$.
Carbon	41·75	41·91	41·83	42·55
Hydrogen	6·70	6·78	6·74	6·39
Oxygen	—	—	51·43	51·06
			100·00	100·00

They possess the same properties, and are most readily obtained in this way.

Oil of Peppermint.

This is the first product of the distillation of the peppermint plant (*Mentha arvensis;* the American plant is *M. piperita*), and amounts on the average to 0·8 per cent. of the total plant used. The crystals of peppermint camphor are obtained from this by cooling, and afterwards exposing the crystals so obtained to the cold night air. The crystals are then drained, and a repetition of the process yields a tolerably pure product.

I obtained a specimen of this oil from Youezana, and made the following experiments with it. The oil had a deep-yellow colour. It was immersed in a freezing mixture of ice and salt for about three hours. At the end of this time a large amount of crystals had separated; the still liquid oil was drained away into another vessel, and a second time exposed to the freezing mixture. In this way a second and a third crop of crystals were obtained, but on the fourth treatment no crystallisation took place.

The oil thus freed from menthol as far as possible was fractionally distilled. About one-fifth distilled over between 198° and 205°, about two-fifths between 206° and 210°, and the remainder between 211° and 216°. Neither of the first two distillates deposited any crystals when immersed in a freezing mixture, but the third liquid formed a gelatinous mass, although no crystals could be collected, as it liquefied again on removal from the freezing mixture.

The first two distillates were almost colourless, the third had a slight yellowish colour. Their specific gravities and specific rotatory powers were:—

	Boiling point.	Sp. gr. at 15°.	Sp. rot. power. Mean of two exp.
1st distillate.....	198—205°.	0·8972	−27·7°
2nd „	206—210	0·8995	−28·7
3rd „	211—216	0·9065	−33·4
Original oil	—	—	−39·5

The first distillate (198—205°) on combustion gave the following numbers:—

1. 0·2338 gram gave 0·6624 gram CO_2 and 0·2622 gram H_2O.
2. 0·2654 „ 0·7502 „ 0·2948 „

	1.	2.	Mean.	Calculated for $C_{10}H_{18}O$.	Calculated for $C_{10}H_{20}O$.
Carbon	77·27	77·09	77·18	77·98	76·92
Hydrogen....	12·46	12·34	12·40	11·70	12·82
Oxygen.....	—	—	10·42	10·32	10·26
			100·00	100·00	100·00

From these numbers it will be seen that this liquid is a mixture of menthol with a body approaching the composition $C_{10}H_{18}$, as suggested by Beckett and Wright (*Chem. Soc. J.*, i, 1, 1876), and from the specific rotatory powers of the different distillates it will be seen that the body $C_{10}H_{18}O$ is inactive, or acts in the opposite direction, as the specific rotatory power increases until in the original oil it is $-39{\cdot}5$. It is not improbable that this substance, which holds the menthol in solution, is the same body as that formed by the action of chromic acid liquor upon the camphor.

I was not, however, able to continue the experiments, as all the time I had to spare was exhausted.

In a note appended to the paper, Prof. Atkinson suggests that menthol is a secondary alcohol derived from a saturated closed chain hydrocarbon formed by the addition of six atoms of hydrogen to ordinary cymene, and that the oxidation-product, $C_{10}H_{18}O$, obtained by Mr. Moriya, is the corresponding ketone.

XVI.—*On the Position taken by the Nitro-group on Nitrating the Dibromotoluenes.*

By R. Nevile and A. Winther.

We have thought it would be interesting to consider the position taken by the nitro-group on acting upon the various dibromotoluenes with strong nitric acid.

Of the six isomeric dibromotoluenes only three give by this reaction mononitro-products. In order to determine the position of the nitro-group in these three we reduced the compound obtained to a dibromotoluidine, and then by substituting bromine for NH_2 by the diazo-perbromide reaction we obtained tribromotoluenes of known constitution (*Chem. Soc. J.*, 1880, 451).

In this manner, from the dibromotoluene 1 : 3 : 4, we obtained a tribromotoluene of m. p. 112—113·6° :—

Analysis :—

Employed .. 0·1937 AgBr = 0·3305 = 72·6 per cent. Br.

Theory for $C_6H_2.CH_3.Br_3$ requires 72·94 per cent. Br,

and from the dibromotoluene 1 : 2 : 5 we obtained a tribromotoluene of m. p. 111·8—112·8° :—

Analysis:—

Employed .. 0·1061 AgBr = 0·1830 = 73·38 per cent. Br.

These agree pretty closely with the tribromotoluene described by us as of constitution 1 : 2 : 4 : 5, and of m. p. 111·2—112·8°. In the first case, then, the nitro-group seems to take a position ortho to CH_3, para to one and meta to the other of the bromine-atoms. In the second case the nitro-group takes a position para to CH_3, ortho to one and meta to the other bromine-atom.

The nitro-compound obtained from dibromotoluene 1 : 2 : 3 gave by similar treatment a mixture of substances from which, by crystallisation from alcohol, we obtained needles of m. p. 38—44°, scales of m. p. 43—58°, and small quantities of a substance only slightly soluble in alcohol, which did not melt at 240°.

The separation of these compounds was so difficult that we were unable accurately to determine whether a mixture of tribromotoluene only was present, or whether tetra- and penta-bromotoluenes produced by an excessive action of the bromine in the perbromide reaction might not also be present.

We may, I think, however, conclude from the two previous examples that bromine as well as CH_3 has a tendency to cause the nitro-group to take up a position para to it, or if the para-position be occupied then an ortho-position; and further, that the combined influence of CH_3 and one bromine-atom can cause the nitro-group to take a position meta to the second bromine-atom.

XVII.—*On Some Derivatives of Toluene and the Toluidines.*

By R. Nevile and A. Winther.

In the course of our investigations into the various isomeric bromine-derivatives of toluene (*Chem. Soc. J.*, 1880, 434) we were obliged to prepare various compounds, from which by an easy step certain other hitherto unknown compounds might very easily be obtained and their constitution determined; and such being the case, we considered it might be of future use to prepare such compounds and to publish the results, in the hope that they might prove useful to others investigating similar compounds.

Bromonitrotoluene ($C_6.CH_3.Br.H.NO_2.H.H$) was prepared from bromonitrotoluidine ($C_6.CH_3.Br.H.NO_2.NH_2.H$) by the removal of the

amido-group with ethyl nitrite. It crystallises in needles of m. p. 74—75°.

Analysis :—

Employed .. 0·1439 AgBr = 0·1250 = 36·96 per cent. Br.

Theory for $C_6H_3.CH_3.Br.NO_2$. requires 37·05 per cent. Br.

By reducing this with tin and hydrochloric acid, we obtained an oily orthobromparatoluidine which solidified in a cooling mixture and then melted at 25—26°.

Analysis :—

Employed .. 0·1224 AgBr = 0·1243 = 43·21 per cent. Br.

Theory for $C_6H_3.CH_3.Br.NH_2$ requires 43·01 per cent. Br.

On the addition of bromine-water to a hydrochloric acid solution of this compound tribromotoluidine ($C_6.CH_3.Br.Br.NH_2.Br.H$) is precipitated. This forms, after purification by crystallisation from alcohol, white needles of m. p. 82·5—83°.

Analysis :—

Employed .. 0·0847 AgBr = 0·1392 = 69·92 per cent. Br.

Theory for $C_6H.CH_3.Br_3.NH_2$ requires 69·76 per cent. Br.

By converting dibromonitrotoluidine ($C_6.CH_3.Br.H.NO_2.NH_2.Br$) of m. p. 125—130° into diazoperbromide and decomposing with glacial acetic acid, we obtained a tribromonitrotoluene ($C_6.CH_3.Br.H.NO_2.Br.Br$) crystallising in white needles, m. p. 105·8—106·8°.

Analysis :—

Employed .. 0·077 AgBr = 0·1163 = 64·26 per cent. Br.

Theory for $C_6H.CH_3.Br_3.NO_2$ requires 64·17 per cent. Br.

By reducing this with iron and acetic acid tribromotoluidine ($C_5.CH_3.Br.H.NH_2.Br.Br$) was obtained. This was separated from undecomposed tribromonitrotoluene by solution in ether, precipitation with strong hydrochloric acid, washing the salt with ether, and finally decomposing it by warm water or sodic carbonate. It was thus obtained as a substance crystallising in needles and melting at 118—118·6°.

Analysis :—

Employed .. 0·0696 AgBr = 0·1144 = 69·93 per cent. Br.

Theory for $C_6HCH_3Br_3NH_2$ = 69·76 per cent. Br.

Dibromoparatoluidine ($C_6.CH_3.Br.H.NH_2.H.Br$) when dissolved in dilute hydrochloric acid gives, on addition of bromine-water, a precipitate of tetrabromoparatoluidine which, after purification, gives white needles of m. p. 226—227°.

1.	2.	3.	4.	5.	6.	
CH_3	NO_2	Br	—	—	—	δ. liquid.
CH_3	NO_2	—	Br	—	—	β. m. p. 44·4—45·2°.
CH_3	NO_2	Br?	—	Br?	—	α. m. p. 55°.
CH_3	—	NO_2	Br	—	—	β. m. p. 31—32°.
CH_3	—	NO_2	—	Br	—	γ. m. p. 81—81·8°.
CH_3	—	NO_2	—	—	Br	δ. m. p. 76·3°.
CH_3	—	—	NO_2	—	Br	δ. m. p. 74—75°.
CH_3	NH_2	Br	—	—	—	δ. liquid.
CH_3	NH_2	—	Br	—	—	β. m. p. 30—32°.
CH_3	NH_2	—	—	Br	—	β. m. p. 55—56°; acetyl compound, m. p. 156—157°.
CH_3	—	NH_2	Br	—	—	γ. m. p. 30—32°; acetyl compound, m. p. 113·7—114·6°.
CH_3	—	NH_2	—	Br	—	γ. m. p. 35·6—36°, acetyl compound, m. p. 167—168°.
CH_3	—	NH_2	—	—	Br	γ. m. p. 78—79°.
CH_3	—	—	NH_2	Br	—	β. liquid; acetyl compound, m. p. 117·5°.
CH_3	—	—	NH_2	—	Br	δ. m. p. 25—26°.
CH_3	NO_2	Br	Br	—	—	β. m. p. 86·6—87·5° (obtained by nitrating dibromotoluene).
CH_3	NO_2?	—	Br	—	Br	δ. m. p. 80—81° " "
CH_3	Br	NO_2	—	Br	—	δ. m. p. 69·5—70·2°.
CH_3	—	NO_2	Br	Br	—	δ. m. p. 62—63·6°.
CH_3	Br	Br	NO_2?	—	NO_2?	δ. m. p. 56·5—57·5° " "
CH_3	Br	—	NO_2	Br	—	δ. m. p. 87—89°.
CH_3	Br	—	NO_2	—	Br	δ. m. p. 56·8—57°.
CH_3	NH_2	Br	Br	—	—	β. m. p. 97—98°.
CH_3	NH_2	Br	—	Br	—	γ. m. p. 45—46°.
CH_3	Br	NH_2	—	Br	—	δ. m. p. 72·5—73·1°; acetyl compound, m. p. 144—145°.
CH_3	Br	NH_2	—	—	Br	δ. m. p. 33—35°.
CH_3	—	NH_2	Br	Br	—	δ. m. p. 58—59°; acetyl compound, m. p. 162—163°.
CH_3	—	NH_2	Br	—	Br	γ. m. p. 74·6—75·5°.
CH_3	—	NH_2	—	Br	Br	δ. m. p. 86·4°; acetyl compound, m. p. 204—205°.
CH_3	Br	Br	NH_2?	—	NH_2?	δ. m. p. 52—53°.
CH_3	Br	—	NH_2	Br	—	δ. m. p. 84·6—85°.
CH_3	Br	—	NH_2	—	Br	δ. m. p. 87—88°.
CH_3	—	Br	NH_2	Br	—	β. m. p. 73°.
CH_3	Br	—	NO_2	Br	Br	δ. m. p. 105·8—106·8°.
CH_3	—	NH_2	Br	Br	Br	δ. m. p. 96—96·8°; acetyl compound, m. p. 171—173°.
CH_3	Br	NH_2	Br	—	Br	γ. m. p. 100—101·6°.
CH_3	Br	NH_2	—	Br	Br	δ. m. p. 93—94°; acetyl compound, m. p. 179—181°.
CH_3	Br	Br	NH_2	Br	—	δ. m. p. 82·5—83°.
CH_3	Br	Br	NH_2	—	Br	δ. m. p. 118—118·6°.
CH_3	Br	NH_2	Br	Br	Br	δ. m. p. 223—224°.
CH_3	Br	Br	NH_2	Br	Br	δ. m. p. 226—227°.
CH_3	NH_2	Br	—	NO_2	—	δ. m. p. 180·3—181·3°.
CH_3	NH_2	NO_2	—	Br	—	γ. m. p. 143°.
CH_3	—	NO_2	NH_2	Br	—	β. m. p. 64—65°; acet. comp., m. p. 210·5°.
CH_3	—	NH_2	NO_2	—	Br	δ. m. p. 179—181°.
CH_3	—	NH_2	—	Br	NO_2	δ. m. p. 87—88°; the quantity of this was too small to get it pure enough for an exact determination of the m. p.
CH_3	Br	—	NO_4	NH_2	Br	δ. m. p. 124—130°.

Analysis :—

Employed .. 0·0968 AgBr = 0·1718 = 75·51 per cent. Br.

Theory for $C_6CH_3Br_4NH_2$ requires 75·65 per cent. Br.

We have thought that it would be convenient to collect together into a table the various bromine-, nitro-, and bromonitro-derivatives of toluene, also the toluidines including both those which we have recently investigated and others, and such a table is subjoined.

We have thus distinguished them :—

α. These have been previously investigated, and we have not investigated them ourselves.

β. These have also been previously investigated, and we have found results agreeing with those previously given.

γ. For these we have obtained and given in this table results differing from those of previous experimenters.

δ. These we believe to have been hitherto undescribed.

We have omitted the various bromotoluenes, as we have previously given a table of them (*Chem. Soc. J.*, 1880, **37**, 451).

XVIII.—*On the Estimation of Nitrogen by Combustion, including the Nitro-compounds.*

By John Ruffle, M.R.A.C., &c.

The amount of nitrogen present in a compound or mixture is usually ascertained by Will and Varrentrap's well known "soda-lime" method; this is easy of execution, and with a little care gives good and often complete results with a great number of substances. It has, however, by various authors been charged with giving somewhat incomplete results when applied to albuminous bodies; moreover it does not estimate the nitrogen of nitric acid at all, and the nitrogen of the other nitrogen oxides frequently escapes detection by it, and at best is but very partially converted into ammonia. In those cases in which nitrogen pentoxide is present, the method will often give results below what it would otherwise furnish, owing to the acid products yielded by the decomposed pentoxide; and this happens to such an extent that even ready-formed ammonia will under such circumstances be only partially determined; whilst if the combustion be so performed that either the substance analysed, or the soda-lime, or both, contain organic matter, all the nitrogen usually correctly estimated will be

obtained in the results, and in addition a portion of the nitro-nitrogen. Should the analysis be repeated, inconstant results will follow.

After very many experiments, in which in turn were employed soda-lime with various gaseous bodies passed over it, the soda-lime mixed with numerous organic and inorganic matters in varying proportions, and the same soda-lime and reagents used alone, the results below quoted were arrived at by the following method:—

A Griffin's ordinary gas combustion furnace was used.

About 1 to 1·5 grams of the substance to be analysed was mixed with 1·5 grams of a mixture containing flowers of sulphur and very finely powdered wood charcoal in equal proportions.

The combustion-tubes used were of iron, 22 inches long, and of $\frac{5}{8}$ths inch internal diameter.

160 grams of sodium hydrate was dissolved in 160 c.c. of hot water; into the hot solution were poured 56 grams of finely powdered calcium oxide, obtained from marble, and well stirred till the slaking was complete; this soda-lime was then thoroughly dried, powdered fine, and preserved in a well stoppered bottle. 21 grams sodium thiosulphate* crystals were crushed fine in an iron mortar, then 18 grams of the above soda-lime added, and intimately intermixed. About 5 grams of this thiosulphate and soda-lime mixture were then introduced into the combustion-tube through a dry and clean funnel, about 30 grams of the thiosulphate and soda-lime mixture were placed in the funnel, and the substance to be analysed lightly but quickly mixed therewith and dropped into the tube, followed by the rest of the thiosulphate and soda-lime mixture. 18 grams of ordinary soda-lime were next poured in, the tube lightly shaken to settle the mass, a good loose plug of asbestos inserted, and the ordinary nitrogen bulb containing a measured quantity of standard acid affixed. The mass in the tube was now 8 inches from the front end of the tube, and the first flame was lit up 4 inches from the front, and thus 4 inches in advance of the mass in the tube; the remainder of the flames were turned up according to evolution of gas through the nitrogen bulb until the whole tube was red hot, and so left for 10 minutes to secure complete combustion of the contents of the tube, the nitrogen bulb then detached, and the acid titrated by standard alkali.

In this way the substance analysed had been burnt in presence of:—

2 mols. of sodium hydrate = 160 } slaked together = 216 ÷ 12 = 18
1 ,, ,, calcium oxide = 56 } exactly
1 ,, ,, crystallised sodic thiosulphate ..... = 248 ÷ 12 = 21
approximately.

* $Na_2S_2O_3$, commonly called "hyposulphite;" but this name belongs properly to the salt $NaHSO_2$, Schützenberger's so-called "hydrosulphite."

If ordinary soda-lime were not placed in front of the thiosulphate mixture some hydric sulphide would be given off during combustion, although so much alkali were present, but with the ordinary soda-lime in front, being made hot before the other contents of the tube, all hydric sulphide was decomposed.

The following results were obtained in addition to others confirmatory, but not quoted. It will be noticed that of the oxides of nitrogen the monoxide, N_2O, is not represented; this is not a common body, and is not important.

The dioxide N_2O_2, or NO, is represented by sodium nitroprusside, $Na_2OFeCy_5(NO)2$ aqua.

The trioxide N_2O_3, is represented by silver nitrite, $Ag_2O.N_2O_3$.

The tetroxide N_2O_4, or NO_2, is represented by picric acid, $C_6H_3(NO_2)_3O$.

The pentoxide N_2O_5, is represented by sodium nitrate, $Na_2O.N_2O_5$.

The sodium nitroprusside containing cyanogen may also be taken to represent many nitrogenous bodies usually converted into ammonia in the ordinary soda-lime process, whilst the albuminous matters are represented and dealt with in the East Indian linseed, &c.:—

	Sodium nitroprusside. $Na_2OFeCy_5NO + 2$ aq., containing nitrogen, 28·18 p. c.	Silver nitrite. $Ag_2ON_2O_3$, containing nitrogen, 8·86 p. c.	Picric acid. $C_6H_3(NO_2)_3O$, containing nitrogen, 18·34 p. c.	Sodium nitrate. $Na_2ON_2O_5$, containing nitrogen, 16·47 p. c.
	28·23	8·58	18·22	16·32
	27·92	—	18·25	16·33
	27·49	—	17·87	16·22
	27·98	—	18·21	16·35
	27·81	—	17·77	16·37
	27·77	—	18·06	16·48
	28·24	—	18·36	16·54
Average ..	27·92	8·58	18·10	16·37

East Indian linseed.		Milk residue.		
Nitrogen by "soda-lime."	Nitrogen by Ruffle's method.	Nitrogen by "soda-lime."	By "soda-lime" containing 5 p. c. sugar.	Nitrogen by Ruffle's method.
3·07	3·39	4·47	4·36	4·89
3·19	3·42	4·46		4·93
Average 3·13	3·40	4·46		4·91

	Dried flesh.		Sample of 14 cargoes of Peruvian guano.	
	Nitrogen by "soda-lime."	Nitrogen by Ruffle's method.	NH_3 by "soda-lime."	NH_3 by Ruffle's method.
	10·03	10·44	4·67	5·03
	10·09	10·38	4·62	4·96
Average..	10·06	10·41	4·64	4·99

Nitrogen pentoxide being present in many substances daily submitted for analysis, a mixture was made of half pure nitrate of soda and half pure sulphate of ammonia, and with it four combustions were made:—

1st. With ordinary soda-lime pure and simple.
2nd. „ „ having 0·5 gram of sugar at end of combustion-tube.
3rd. With ordinary soda-lime mixed with 5 per cent. sugar, and with 0·5 gram sugar at end.
4th. By the new method.

The results obtained were:—

	Per cent.		Per cent.
Sulphate of ammonia containing nitrogen....	21·21 ÷ 2	=	10·60
Nitrate of soda „ „	16·47 „	=	8·23
			18·83

1st.	2nd.	3rd.	4th.
9·17	9·59	12·68	18·76

From this it will be seen that the soda-lime pure and simple did not yield even the nitrogen of the ready formed ammonia (9·17 out of 10·60, a deficiency of 1·53 per cent.) neither did it if organic matter were at end of the tube (9·59 out of 10·60, a deficiency of 1·01 per cent.); and if the soda-lime contained organic matter the result was above the ready-formed ammonia, and far short of the total nitrogen, 12·68 per cent. against 10·60 in the one case, and 12·68 against 18·83 in the other. The new method, however, gives practically complete results, 18·76 against 18·83, and these striking results were confirmed by numerous other analyses performed in course of the research.

It will be an assistance to see the superiority of the new reaction if we compare the above results obtained with sodium nitroprusside, picric acid, and sodium nitrate, with some results by the same salts burnt with ordinary soda-lime pure and simple, and the same containing 10 per cent. sugar:—

	Nitrogen by "soda-lime" only.	Nitrogen by "soda-lime," with 10 p. c. sugar.
Sodium nitroprusside.....	23·88	26·29
Picric acid	10·35	12·54
Sodium nitrate	acid given off	8·00

It frequently happens that a reaction generally successful has yet on some occasions to be specially applied; it is so in one instance with the present case: a chemist receiving an ordinary artificial manure and preparing it for analysis commonly reduces it to a pasty mass. If a portion of this be taken, and either cut up fine or dried in the water-oven and powdered, and a combustion made with it as directed on page 88, results will be obtained below the truth; for instance, some samples of superphosphate containing 25 per cent. nitrate of soda = 4·11 per cent. nitrogen.

Cut up.		Dried at 100°.	
1st sample	3·37	7th sample	3·82
2nd „	3·54	8th „	3·50
3rd „	3·50	9th „	3·53
4th „	3·66		
5th „	3·38		
6th „	3·62		

The obstacle to success is doubtless the layer of calcic sulphate with which the particles of nitrogenous matter become covered in the beating up of the sample, thus preventing the due contact of the thiosulphite and soda-lime mixture with the substance; sodium thiosulphate is, however, in a strongly saturated solution found to be a solvent for calcium sulphate, and by mixing the pasty artificial manure with its own weight of sodium thiosulphate crystals, well pounding the same together in a mortar, weighing off a portion of this mass spread out on a watch glass, leaving it in the water-oven for a couple of hours at 100° C. weighing to ascertain the loss, then powdering, and using 3—4 grams for a combustion with "hyposulphite and soda-lime mixture," as before directed, full results will be arrived at; thus the following determinations were made in some prepared samples of manures, and were confirmed by many others not here published:—

Superphosphate containing—

25 p. c. sodium nitrate = 4·11 p. c. nitrogen gave ..	4·22 p. c.
	4·25 „
	4·23 „
	4·05 „
20 p. c. sodium nitrate = 3·29 p. c. nitrogen gave ..	3·17 „
	3·18 „
25 p. c. ammonium nitrate = 8·75 p. c. nitrogen gave	8·98 „
	8·81 „

The new method is essentially one of reduction by a very powerful deoxidiser in presence of a strong alkali. The salt commonly called "hyposulphite of soda" may be viewed as the acid sodium salt of the monoxide of sulphur [$S_2O_3Na_2 = Na_2O,2SO$]. The crystals of this cannot be brought in contact with pure alkali without forming immediately an impracticable wet mass, the soda-lime of 2 mols. sodium hydrate and 1 mol. of calcium oxide is strictly but a device to conveniently convey enough alkali to the acid monoxide to form the mono-acid sodium salt of the monoxide of sulphur, a body not yet formed and isolated. When this salt is formed *it* will probably be found performing the complete analysis, will be a salt of alkaline reaction, and crystallise with 7 mols. of water; meanwhile the method as described only leaves the "soda" and "hyposulphite" in contact and not combined, and the results are a trifle below the theoretical quantity.

The reactions above quoted warrant the employment of this method for all combustions. The "anilines" are by this process attacked to complete decomposition, but are not estimated.

To clean out the combustion-tube after use, provide an iron rod, say $\frac{3}{8}$ths inch diameter and 2 feet long; when the last tap is turned on lay the rod lengthwise over the flame to get hot; at close of combustion remove the nitrogen bulb and cork, draw out the asbestos, and whilst the tube is cooling, insert the rod two or three times from front to back. When the tube is cold, pour water in, leave the whole at rest for an hour, then agitate the water by repeatedly drawing the rod up and down, pour out the dirty water, refill, agitate, &c., doing this till the wash water comes out clean; if warm water be used the cleansing will be much quickened. When the tube is clean, heat it for a minute to dryness in the furnace, and it will be ready for re-use.

Precautions:—

(*a.*) Use ordinary soda-lime where directed.

(*b.*) Light up first flame 4 inches in advance of the mass, and keep it red hot, so that the mass shall not set in fore part of tube.

XIX.—*On the Estimation of Organic Carbon in Air.*

By A. Dupré, Ph.D., F.R.S., Lecturer on Chemistry at Westminster Hospital, and H. Wilson Hake, Ph.D., F.C.S., Lecturer on Chemistry and Physics at Queenwood College, Hants.

In a former paper (*Chem. Soc. J.*, March, 1879) we demonstrated the possibility of estimating gravimetrically minute quantities of carbon or carbonic acid in a manner not previously attempted, the process possessing, in our opinion, certain advantages which made it applicable in cases where other methods might be inconvenient or inadequate.

We suggested, among other applications of the process, that it might prove useful for the estimation of carbonic acid and of volatile and suspended organic matter in air. With this particular end in view a series of experiments were made, the details of which we beg to lay before the Society.

The process for the estimation of carbon consisted, it will be remembered, in burning the known quantity of carbonaceous matter in a current of oxygen, absorbing the carbonic anhydride so formed in baryta-water, and converting the resulting baric carbonate into baric sulphate, a final product being thus obtained which weighs nearly twenty times (19·4 exactly) as much as the carbon originally dealt with. The various precautions necessary to prevent the introduction of extraneous carbonic acid, and the successive steps of the process, are described at length in the former paper already referred to.

In a long series of preliminary experiments, air, after filtration through cotton wool, was passed first through an absorption tube containing baryta-water, next over oxide of copper heated to redness in a porcelain tube, and finally through a second absorption tube, also containing baryta-water, basic lead acetate solution being sometimes substituted for the baryta-water in the second absorption tube. In several of the experiments the presence of organic matter was demonstrated, sometimes in not inconsiderable quantity, at other times in minute traces only. It appeared to us probable that at least part of the organic matter might be arrested and lost in its passage through the first absorption tube. It became necessary, therefore, to devise an arrangement of the apparatus by which this previous absorption of the organic matter should be avoided. The following arrangement was at last adopted:—

The filtered air, which to begin with was conducted by means of metal tubing, but afterwards by glass tubing, from its particular

source into the laboratory, was then divided into two currents by means of a **T**-piece attached to the end of the tube. From this **T**-piece connections by means of glass tubing were made with the Pettenkofer absorption tubes. In the one case the connection was direct between the **T**-piece and the absorption tube, in the other the air was compelled to pass through a porcelain tube containing cupric oxide heated to redness in a combustion furnace, and then immediately into an absorption tube. Each absorption tube was connected by means of caoutchouc tubing with a meter* capable of measuring accurately to within a cubic inch, and each meter, by means of a caoutchouc tube carrying a screw pinchcock, with a common flask, from which the air was being continually exhausted by a water pump. The air-currents could thus be regulated to a nicety, so that approximately equal quantities of air could be passed through each absorption tube in equal times. The rate of passage of the air was from two to three litres per hour.

The object to be gained by this arrangement will be obvious. The baric carbonate obtained in the one tube is due to the carbonic acid of the air only, that obtained in the other being due to carbonic acid of the air *plus* any carbonic acid due to the combustion of other forms of carbon. The baric carbonate being next converted into baric sulphate, the excess of baric sulphate obtained from the tube intended for the estimation of the organic carbon over that obtained from the other tube would be a measure of the organic carbon present in the air under examination.

The apparatus being then at last arranged in the manner just described, several experiments were made, and in all cases without exception an excess of baric sulphate was obtained from the tube intended for the estimation of the organic matter. Of these experiments, five estimations were made with the air of one of the yards of Westminster Hospital, and one with the air in the laboratory while the combustion furnace was in use, the other estimations being purposely made with impure air. A clearer view of their tendency will be best arrived at after an examination of the actual figures obtained, which are as follows (see p. 95).

The greatest quantity of air used in any experiment did not exceed 16 litres, as little as $4\frac{1}{2}$ litres being used in some cases. In Experiments 1, 2, and 6, a metal tube about 30 feet long was used to conduct the air from the yard, but as this was found to absorb carbonic acid to a large extent, glass tubing joined by wired caoutchouc tubing was sub-

* Some care is necessary in the use of these meters. Not only should they be carefully tested by a standard measure, but this testing must be conducted under conditions as regards speed and pressure of air current as nearly as possible the same as those under which the experiments are afterwards carried on.

	Temperature.	Date.	1st Current. No. of c.c. used in current for CO_2 only.	2nd Current. No. of c.c. used in current for organic C.	Carbon obtained from 1st current.	Carbon obtained from 2nd current.	10,000 c.c. air contain—		Remarks.
							C as CO_2.*	C in other forms.	
1. Air of yard	—	Oct. 16, 1880	12,463	12,387	·000773	·000933	·00062	·00014	1. Metal tubing
2. „ „	—	Oct. 18, 1880	11,688	11,888	·001592	·001737	·00136	·00010	2. „ „
3. „ „	—	Oct. 25, 1880	12,681	12,253	·003628	·003783	·00286	·00023	3. Glass tubing
4. „ „	1° C.	Jan. 13, 1881	6,846	6,783	·004469	·00457	·00653	·00021	4. „ „
5. „ „	−2° C.	Jan. 17, 1881	15,959	15,802	·004412	·004536	·00276	·00011	5. „ „
6. „ laboratory .	12° C.	Jan. 11, 1881	4,549	4,502	·00477	·00478	·01048	·00023	6. Metal tubing
7. „ dust-hole ..	—	Oct. 19, 1880	13,720	13,522	·001886	·002242	·00137	·00028	7. Glass tubing
8. „ coal sack ..	5° C.	Nov. 3, 1880	—	9,136	lost	·004015	—	—	8. „ „
9. „ „ ..	—	Nov. 9, 1880	11,453	11,469	·00356	·00368	·00311	·00010	9. „ „
10. „ coal box...	10° C.	Nov. 11, 1880	4,520	4,528	·00320	·00683	·00708	·00800	10. „ „

* The No. of mgrms. C × 1·866 = No. of c.c. CO_2 in 10,000 c.c. air.

stituted throughout all the other experiments. All joints of glass tubing were made with the greatest care, and in such a manner that one tube fitted some little distance into the one next to it. The large quantity of carbonic acid obtained in Experiment 6 was due to the fact that the combustion furnace and several Bunsen burners were alight in the room from which the air was taken.

In Experiment 8 an accident prevented the estimation of the carbonic acid, and therefore of the organic matter. The air was obtained in this experiment by plunging an iron pipe down the centre of the sack, and so breaking up some of the lumps, and connecting this tube with the air-tube leading to the laboratory. Experiment 9 was a repetition of Experiment 8, the arrangement having been left intact after an interval of 24 hours, but oxidation or diffusion having taken place, the amount of organic matter indicated was very small. Experiment 10 was an extended repetition of Experiment 8. The coal in the box weighed about 80 lbs., and was broken up into small lumps shortly before the commencement of the experiment. An iron tube, passed down the centre through a hole in the lid, was connected with the air-tube leading to the laboratory. A considerable quantity of organic matter was obtained.

In Experiments 1, 2, 3, 7,* 8, 9, and 10 the air was filtered through a chloride of calcium tube, 6 inches long, which was filled, one-half with fibrous and freshly ignited asbestos, the other half with cotton wool. In Experiments 4, 5, and 6 the filter-tube was filled with previously ignited asbestos only. It may be mentioned that no error seems to have been introduced by the use of cotton wool through oxidation of possible organic matter contained in it.

These experiments demonstrate the presence in the air of London of a small, but by our method appreciable and estimable quantity of carbon in other forms than that of carbonic acid, presumably in fact in the form of so-called organic carbon in some compound or compounds of a volatile nature, not as suspended matter. The importance of this fact cannot be too strongly emphasised. Berzelius, nearly fifty years ago, alluding to some experiments in this direction, says that such an investigation being once possible, deserves to be frequently repeated under varying conditions and at different seasons of the year (*Berzelius Jahresb.*, 1835, **22**, 47).

The bearing of these results on air analysis, especially in relation to physiological and sanitary investigations, will be seen presently. That the method is applicable to the accurate estimation of carbonic acid in air is sufficiently obvious. That it may advantageously be applied to the determination of carbonic acid and fire-damp in coal

* In reference to Experiment 7, it should be mentioned that the air in the dust-hole had but little smell at the time.

mines is suggested by Experiments 7—10. Experiment 4, which was made during a moderate fog, seems to indicate that the quantity of carbonic acid in the air is much higher during the prevalence of this phenomenon than ordinarily, and further experiments in this direction would be not without interest.

We have not as yet attempted to estimate the suspended organic matter in air by this method, as owing to the position of the laboratory good results could not be expected. The possibility of so doing is clear. We propose to filter the air through a porcelain tube filled partly with asbestos, partly with cupric oxide, the tube so filled being previously ignited in a current of oxygen. The subsequent combustion and estimation of the carbonaceous matter thus arrested could be effected by our method, essentially as described on page 3 of our former paper. The summer months would, as far as London or any large town is concerned, be obviously better suited to such an investigation.

The presence of organic matter in air, and especially in the air of towns, crowded Law Courts, and sick rooms, has long been considered indisputable, many chemists having succeeded in detecting it. We cannot and do not, therefore, claim any priority on this head. Moreover, more work has been done in this direction than appears at first sight. In one or two instances we observe a similarity of intention to the method employed by us, a similarity which is, however, far from being an identity.

As early as 1835 Boussingault (*Compt. rend.*, **1**, 87), who had previously estimated hydrogen in atmospheric air, describes the following experiment:—On August 5th, 1835, in the Court of the University of Lyon, 205 litres of air weighing 237·5 grams, when corrected for temperature and pressure, were first completely deprived of their carbonic acid by passage through a strong solution of caustic potash. The air was then caused to pass successively through two flasks containing baryta-water, a glass tube filled with copper turnings and heated to redness, and finally through a third flask containing baryta-water. The baryta-water in the second flask remained perfectly bright and clear, that in the third flask showing a marked turbidity. The baric carbonate in this flask converted into baric sulphate weighed, says Boussingault, 0·685 gram, corresponding to 0·13 gram CO_2, and consequently 0·031 gram C. The air in Lyon he concludes contains therefore 0·00012 of its weight of carbon, not in the form of carbonic acid.

No further experiments appear to have been made by Boussingault, and no precautions in dealing with his baric carbonate are made mention of by him. His figure is more than ten times in excess of our average result. The organic carbon found by him in the air would

be nearly equal to the amount of carbon combined as carbonic acid. The rate of passage of the air was very rapid. The introduction of extraneous carbonic acid cannot, we have found, be avoided in such an experiment without extreme precautions. All things considered, we cannot help regarding his estimation as fallacious. It is to be regretted that his research was discontinued.

About the same year as Boussingault, de Saussure found that when 2,000 vols. of atmospheric air, freed from carbonic acid and mixed with pure hydrogen, were exploded by the electric spark, 1 per cent. by volume of carbonic acid was formed, which he attributes to the presence of carbonic oxide in the air. What is meant by this it is difficult to say.

Chevallier also points out the presence of organic matter in the air in Paris.

Vogel (1835, Erdmann, *J. pr. Chem.*, **4**, 239) repeated an expement made by Moscati by condensing the mixture in the air of a lecture-room on cold clean surfaces, and found in the water so formed no chlorine, but germs, and an organic substance which reduced nitrate of silver in solution when exposed to the light. He shows further that this result is not due to human breath, and disputes de Saussure's hypothesis of carbonic oxide.

Verver (*Berzelius Jahresb.*, 1835, **22**, 46) estimated both hydrogen and carbon in air, and found, as the mean of several experiments, 0·144 theoretical volume of C. in 1,000 vols. of air. A tabular view of his and Boussingault's results compared with our own is as follows:—

Boussingault found	in 10 litres	of air	0·00193	gram C.
Verser	„	„	0·00154	„
We find		„	0·000154	„

Verver's results are thus seen to be nearly as high as Boussingault's figure. Without doubt the same criticism applies to his experiments as to Boussingault's solitary one, since they are a distinct repetition of the Lyon experiment.

Pettenkofer (1863, "Ueber die Respiration," *Ann. Chem. Pharm.*, Suppl. **2**, 1—70) suggests in his research on respiration a method for determining H and CH_4 in air by passing the air simultaneously through two absorption tubes containing baryta-water in essentially the same manner as adopted by us, with the difference, that his air is not filtered, and that instead of cupric oxide, he uses spongy platinum, and that he estimates his baric carbonate by his well-known method of titrating a portion of the residual baryta-water with oxalic acid. The excess of carbonic acid, and of water formed not due to moisture, give him a measure of the organic carbon and hydrogen

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contained in the air under examination. He applies this process, however, only to the air which leaves his apparatus, and on the expressed assumption that the air entering the apparatus is "free from any combustible H or C compound;" an assumption which ignores the experiments of Boussingault, Verver, &c., just detailed. Considering the enormous quantities of air used by Pettenkofer, in most cases exceeding 8,000 litres per hour, the correction necessary, even calculating 0·000015 gram organic C in 1 litre, becomes of a very grave character, and would apparently amount in some cases to the whole of the organic carbon found.*

The experiments of Angus Smith ("Air and Rain," 399) and the more recent experiments of H. Macagno (*Chem. News*, **41**, 47), which have for their object the estimations of organic matter in unfiltered air by the decolorisation of permanganate of potash, can only be considered as approximations, and though of interest and importance, have nothing in common with our methods. The methods of Angus Smith and of Hugo v. Gilm for the estimation of carbonic acid in air have already been referred to and discussed in our former paper. Finally, reference should be made to two interesting papers by H. Karsten (*Pogg. Ann.*, **109**, 346, and **115**, 343), who finds that starch, wax, sugar, finely-divided carbon, &c., oxidise slowly at ordinary temperatures, and that a vulcanised caoutchouc tube 8 metres long, 0·005 metre internal diameter, gave 0·0006 gram CO_2 when during about 10 days 20 litres of moist air free from CO_2 were passed through it; an experiment which conclusively shows that no error can have been introduced by the use of caoutchouc connections by us in the manner already described.

* At the minimum amount of ventilation of 8,000 litres per hour the amount of organic carbon contained in the air passing through the apparatus in 24 hours (taking the mean of our experiments 0·000154 gram C. per 10 litres as basis) would be equivalent to 3·96 grams marsh-gas, or almost exactly the amount found by Pettenkofer and Voit in Experiment 4. A ventilation of 13,000 litres per hour would be sufficient to account for the maximum amount of marsh-gas found, viz., 6·3 grams, in Experiment 2. It is obvious, therefore, that the question as to the presence of marsh-gas in the gases of respiration is by no means established by Pettenkofer and Voit's experiments.

XX.—*On the Action of the Copper-zinc Couple upon Nitrates and the Estimation of Nitric Acid in Water Analysis.*

By M. Whitley Williams.

While analysing some natural waters, I lately had occasion to make many estimations of the nitric acid in them; and as I had previously been familiar with the uses of Gladstone and Tribe's "copper-zinc couple," I determined to apply it to this purpose.

It is well known that T. E. Thorpe has already described a method of estimating nitric acid in water analysis by means of the "couple," in which the water is first evaporated to dryness, and the residue, dissolved in water, is boiled with lime, and then distilled with copper-coated zinc until no more ammonia is evolved. The ammonia is condensed in hydrochloric acid, and titrated by Nessler's method. This proceeding appeared to me to be little if at all simpler than the well-known processes previously employed for reducing nitrates to ammonia by means of aluminium or of zinc and iron, its only advantage being that the use of caustic alkali (which itself frequently contains nitrate) is avoided. The ammonia requires collection by distillation in this, just as in the aluminium and zinc-iron methods. There is, moreover, a theoretical objection to *boiling* a nitrate with the couple; for it was observed by Thorpe himself that ammonium nitrate evolved nitric oxide when thus treated.

Seeking for a safer and more simple method of using the copper-zinc couple, I noticed that Gladstone and Tribe, in their experiments upon the reduction of nitre in the cold, did not distil the ammonia, but titrated it directly in a measured quantity of solution decanted from the couple. Like Thorpe, these authors also noticed that ammonium nitrate evolved nitric oxide when boiled with the couple; but they made the important additional observation, that no decomposition of this kind occurred when the reduction was performed at the ordinary atmospheric temperature, but that the whole of the nitric acid was then converted into ammonia. The accuracy of Gladstone and Tribe's final results convinced me that the method of operation adopted in their experiments could be used to determine the nitrates in natural waters. I therefore tried it for the analyses above referred to, and found that when properly applied it yielded very satisfactory results.

While making the analyses by this method, I observed that the times required for the conversion of similar quantities of nitric acid into ammonia under apparently similar conditions were by no means equal in different waters. In some of the waters a relatively large amount of nitric acid was completely reduced in a short time; while in others, with a much smaller amount of nitric acid, the reduction

occupied a longer time. It appeared as though the various salts present in the waters exercised some influence upon the duration of the reaction. These observations and a desire to shorten the process and render it more certain induced me to make a series of experiments to ascertain the influence of temperature and of various chemical agents upon the course of the reaction. The experiments not only accounted for the peculiarities I had noticed, but brought to light some facts which have an interesting bearing upon the theory of the reaction, and an important application to the estimation of nitrates by means of the copper-zinc couple. I purpose in this paper, first to give an account of these experiments, and then to describe their application to the analysis of nitrates.

Reduction of Nitric Acid by the Copper-zinc Couple under various Conditions.

Messrs. Gladstone and Tribe have shown that ammonia and nitrite of potassium are produced from the beginning of the reaction, when the copper-zinc couple acts in the cold upon a dilute solution of nitre. As the reaction progresses both these bodies increase in amount; the nitrite next decreases, and finally disappears altogether, the whole of the nitrogen of the nitric acid being then found in the form of ammonia (*Chem. Soc. J.*, 1878, Trans., 140). If the formation of nitrite be a true intermediate stage of the whole reaction, it might be expected that the nitrate would all be reduced to nitrite before any ammonia was produced; but, although ammonia appears at the very beginning of the reaction, it is probable that it arises, not from any direct transformation of the nitric acid into ammonia, but from a further action of the couple upon nitrite (the nitrate in the immediate vicinity being exhausted), which has not had time to escape from the meshes of the spongy deposit of copper before it is attacked. If this view be correct, it follows that less ammonia and more nitrite would be produced the more concentrated the solution of nitre employed, because the nitrate solution in immediate contact with the couple would then be less quickly exhausted. I have ascertained by direct experiments that this is precisely what happens. It therefore seems fair to conclude that the whole of the nitrate passes through the stage of nitrite before transformation into ammonia. It is important to remember this phase of the reaction in considering the results of the experiments I am about to describe, since the great variations they show in the course and duration of the reaction are most probably due to influences exerted upon the nitrite.*

The experiments, being intended to bear upon water analysis, were

* No hyponitrous acid can be found at any stage, nitrous acid being the only intermediate body that has been noticed.

made upon solutions the concentration of which was not greater than that of the nitrates commonly met with in natural waters. A solution of nitre was employed, and it was digested upon a constant amount of copper-zinc couple at the temperatures given, and with the addition of the various acids, alkalis, and salts mentioned, under each experiment. The progress of the reaction was ascertained at stated intervals by withdrawing portions of the solutions and determining the amounts of nitrous acid and ammonia that were present. The ammonia was estimated by directly titrating a measured quantity of the withdrawn fluid by Nessler's method; and the nitrous acid was determined in a similar manner by the colorimetric method recently proposed by Peter Griess, which depends upon the coloration developed by the action of nitrous acid upon metaphenylenediamine in an acid solution. Very accurate results can be obtained by this process. I have found it advisable for the two solutions compared to be at the same temperature, because the yellow coloration develops more rapidly in warm than in cold solutions. There are other conditions affecting the rate at which the colour is developed, but these are of a chemical nature and not easily controlled.

All the experiments were conducted in as nearly the same manner as possible, in order that the results might be comparable. Each experiment was made in the following manner: Three strips of zinc-foil, 6 cm. wide and 20 cm. long, were creased to render them rigid, and placed in a large-mouthed stoppered bottle of rather more than one litre capacity. They stretched from the bottom quite to the top of the bottle, and pressed against the sides, so that they did not rub each other when the bottle was moved. To make the zinc into couple, the bottle was filled with a solution of copper sulphate containing about 3 per cent. of the crystallised salt, and was allowed to stand until the zinc had acquired a copious firmly adherent deposit of black copper. The couple was then gently washed until free from zinc sulphate, care being taken to detach as little as possible of the spongy deposit of copper. The adhering distilled water was finally displaced by washing with some of the solution to be experimented upon, and the bottle filled up with a further quantity of the same solution. The stopper was then inserted, and the solution allowed to digest at the temperature and under the conditions mentioned under each experiment. In all the experiments made at 24° C., the temperature was maintained constant day and night by partially immersing the bottles in a large bath of water kept uniformly warm by a small gas-flame, which was controlled by an automatic mercurial thermostat immersed in the water. The results are stated in parts per hundred thousand, and the numbers given in the tables are generally the means of several titrations.

Experiment I.—A solution of nitre containing 10 parts in 100,000 of distilled water was employed in this experiment. The temperature varied: it was that of the atmosphere at the time, and during parts of the experiment was only a few degrees above the freezing point.

Times	2 hours.	5 hours.	10 hours.	20 hours.	50 hours.	70 hours.
NO_2.....	0·78	2·24	2·34	2·27	0·76	trace
NH_3.....	0·196	0·324	0·380	0·538	0·856	1·672

The theoretical amount of ammonia equivalent to 10 parts of KNO_3, is 1·685 parts per hundred thousand; it will, therefore, be noticed that the reduction was hardly concluded after 70 hours' digestion at the low temperature at which the experiment was made. The reaction shows a peculiar course; from the fifth to the twentieth hour its progress is exceedingly slow, and after that it becomes more and more rapid towards the end. Messrs. Gladstone and Tribe observed the same unaccountable behaviour with much stronger solutions of nitre, and their experiments also were made at somewhat low temperatures. They point out that "the reaction starts somewhat energetically, then diminishes considerably, again increases, and finally ends more energetically than it began."

Experiment II.—This experiment was precisely the same as the first, with the exception, that the temperature throughout was maintained constant at 24° C.

Times	1 hour.	2 hours.	5 hours.	10 hours.	20 hours.
NO_2.....	0·58	0·52	0·08	trace	nil
NH_3.....	0·512	0·790	1·20	1·66	1·69

Comparing these figures with the former ones, it will be seen that at 24° the reaction is nearly completed in 10 hours, and that the quiescent stage has either disappeared altogether, or only the merest traces of it are left in the interval between the first and second hours. The energy of the reaction diminishes pretty regularly from the commencement to the end, and it will be noticed that a much smaller quantity of nitrite is to be found. It is impossible to say whether the diminution in the nitrite is due to its being attacked by hydrogen more readily at the higher temperature, or whether it is merely due to increased activity of the couple in decomposing water. In the latter case more of the nitrite would be immediately transformed into ammonia within the meshes of the spongy copper than would be so

transformed when the couple is less active at the lower temperature. In one of their earlier papers, Messrs. Gladstone and Tribe showed that the couple evolved hydrogen from distilled water in a rapidly increasing ratio as the temperature was raised. At temperatures near the freezing point, they found, in fact, that the evolution of hydrogen nearly ceased altogether.

Experiment III.—Same strength of the nitre solution as in I. Before pouring it upon the couple it was about half saturated with carbonic acid gas. Temperature 24°.

Times	1 hour.	2 hours.	5 hours.	10 hours.
NO_2.....	0·06	0·02	nil	nil
NH_3.....	1·10	1·65	1·69	1·684

The last figure is the mean of sixteen very carefully made titrations. This experiment revealed an unexpected and very useful influence of carbonic acid. Compared with the figures of I and II, these show that carbonic acid has an influence similar to that of heat, but more energetic. The accumulation of nitrite in the solution is almost entirely prevented, and the reduction is accomplished with surprising rapidity, being very nearly finished at the second hour. The action of the carbonic acid is two-fold; it tends to decompose the nitrite with liberation of nitrous acid, and it also combines with the ammonia and caustic potash produced in the reaction, which would otherwise tend by their presence to preserve the nitrite, as the subsequent experiments show.

Experiment IV.—Same strength of nitre solution. Each litre contained 4 grams NaHO (pure, prepared from sodium). Temperature 24°.

Times	1 hour.	2 hours.	5 hours.	10 hours.	20 hours.
NO_2.....	0·82	·0·22	0·18	0·02	nil
NH_3.....	0·97	1·23	1·63	1·68	1·69

It appears from these numbers that caustic soda at first accelerates the reaction considerably, but afterwards retards its conclusion. In Experiment II a much greater reduction occurs between the fifth and twentieth hour than in this. The concentration of alkali used in this experiment is about that which produces the maximum acceleration in the rate of evolution of hydrogen by the couple (Gladstone and Tribe, *Chem. Soc. J.*, 1878, Trans., 141).

Experiment V.—Same strength of nitre. Each litre of the solution contained 6 grams Na_2CO_3. Temperature 24°.

Times	1 hour.	2 hours.	5 hours.	12 hours.	20 hours.
NO_2.....	0·85	1·13	0·97	0·06	trace
NH_3.....	0·29	0·59	1·22	1·62	1·68

Here a decided retardation of the reaction is to be observed. The formation of ammonia is hindered, and nitrite accumulates in the solution, but to a greater extent in this than in the preceding experiment. Both these experiments indicate the tendency of alkali to preserve the nitrite, but the carbonate has a greater effect than the equivalent amount of the caustic alkali. The last traces of nitrite seem to be destroyed with great difficulty in presence of these bodies.

Experiment VI.—Same strength of nitre, saturated with lime. Temperature 24°.

Times	1 hour.	2 hours.	12 hours.	20 hours.	37 hours.
NO_2.....	0·98	1·38	1·77	1·30	0·61
NH_3.....	0·34	0·44	1·03	1·18	—

The reaction is here greatly retarded, it was yet far from completion when the experiment was stopped. It will be noticed that nitrite accumulates in the solution as with the other alkalis. Thorpe noticed that lime added to a solution of nitre and distilled from the couple, caused the ammonia to distil more quickly than when the nitre was distilled alone; but he did not attribute this effect to any influence of the lime upon the duration of the reaction.

Experiment VII.—Same strength of nitre, saturated with pure precipitated calcium sulphate. Temperature 24°.

Times	2 hours.	5 hours.	10 hours.
NO_2.....	1·48	0·18	nil
NH_3.....	0·65	1·32	1·68

The presence of sulphate of lime appears to be favourable to the reaction. A larger proportion of nitrite is formed in the early part than with nitre alone, but there is no evident tendency to its preservation, and the reaction accordingly comes to an earlier close.

Experiment VIII.—Same strength of nitre with one-tenth of a per cent. of sodium chloride added. Temperature 24°.

Times	1 hour.	2 hours.	5 hours.	12 hours.
NO_3.. ...	0·17	0·09	—	nil
NH_3.....	0·98	1·31	—	1·68

The end was probably reached about the fifth hour, or at least long before the twelfth, but no observation was made at that time.

The reaction is expedited by salt almost as much as by carbonic acid, an effect which must be ascribed to more rapid decomposition of water by the couple. It would probably be found that the couple evolves hydrogen gas more rapidly from a saline solution than from pure water.

Experiment IX.—Same strength of nitre with addition of one-tenth per cent. of phosphoric acid (H_3PO_4).

Times	1 hour.	2 hours.	2 days.	23 days.	44 days.
NO_3.....	traces	nil	nil	nil	nil
NH_3.....	1·55	1·67	0·8	0·1	0·04

The reaction is completed within two hours. The amount of ammonia found in solution at the end of the second hour did not quite reach the theoretical quantity. It had probably already begun to decrease, and on further standing, rapidly grew less. In two days only about half of it remained, and in time it nearly all disappeared. This was due to the formation of an insoluble ammoniacal compound, for ammonia was yielded in quantity by the residue of the couple when it was treated with a perfectly pure soda solution. The compound was probably a double phosphate of zinc and ammonia, analogous to the well-known ammonio-magnesium phosphate.

Experiments have been made to ascertain the influence of other acids, both organic and inorganic, upon the course of the reaction, with the same general result, that nitrous acid was formed or rather accumulated, only to a slight extent, and the reduction to ammonia was quickly accomplished. Very small quantities of acid were required to produce these effects.

Experiment X.—A very hard chalk water was found to contain nitrates equivalent to about 5 parts NO_3 in 100,000. Its temporary hardness was over 20 degrees, and it contained 49 parts of mineral matter. It was examined in a manner similar to that adopted in the preceding experiments. Temperature 15—19°.

Times	30 mins.	1 hour.	2 hours.	5 hours.	20 hours.	23 hours.
NO_2.....	0·34	0·58	0·75	0·51	0·03	nil
NH_3.....	0·16	0·34	0·50	1·25	1·36	1·38

1·38 NH_3 corresponds to 5·03 NO_3 in 100,000. This water was strongly alkaline with dissolved carbonate of lime, the retarding effect of which is seen to be analogous to that of sodium carbonate shown in Experiment V. The addition to this water of 3 per cent. of a saturated solution of sodium carbonate caused the nitrites to rise to 1·86 NO_2 in five hours, while the formation of ammonia had been so greatly retarded that only 0·48 was found at the same period. This water took about as long a time for complete reduction of the nitrates as any water I have examined. It must be noticed, however, that the temperature was lower than that maintained during the preceding experiments.

It is evident that the peculiarities of behaviour observed in reducing the nitrates in natural waters by the copper-zinc couple are fully accounted for by the accelerating influence of acids and neutral salts, and the retarding effect of alkalis and alkaline salts shown in the foregoing series of experiments. Of the various salts occurring in natural waters, each produces its particular effect, and so an endless variety is found in the course taken by the reaction when these waters are acted upon by the couple under apparently identical conditions. Perhaps the most potent agents in modifying the speed of the reaction are free carbonic acid and carbonate of lime, both of which are so generally found in waters. But these experiments also indicate the means of hastening the reduction without imperilling the accuracy of the analysis, so that the rapidity of the copper-zinc couple process becomes quite independent of any retarding influences that may be exerted by the substances naturally present in the water.

The Estimation of Nitric Acid in Water Analysis.

The method used in the experiments just described can be applied to the estimation of nitric acid in water analysis, but it is obvious that there is a limit to its application, dependent upon the maximum dilution of ammonia which can be directly titrated with accuracy by Nessler's process. To determine this limit and to ascertain the rate of reduction in very dilute solutions of nitre, the following three experiments were made, the method of experiment being precisely similar to that employed in the above series.

Experiment XI.—Solution of nitre containing 1 part in 100,000. Temperature varied about 10°.

Times	2 hours.	5 hours.	20 hours.	30 hours.
NO_2.....	0·028	0·032	trace	nil
NH_3.....	0·13	0·16	0·16	0·17

Experiment XII.—Same as XI, but temperature 24°.

Times	1 hour.	2 hours.	5 hours.	10 hours.	20 hours.
NO_2.....	trace	trace	trace	trace	nil
NH_3.....	0 074	0·13	0·148	0·157	0·168

The theoretical amount of ammonia is 0·1685.

Experiment XIII.—0·2 nitre in 100,000. Temperature 24°.

Times	1 hour.	4 hours.	10 hours.
NO_2.....	trace	trace	nil
NH_3.....	0·02	0·032	0·0334

The theoretical amount of ammonia is 0·0337. To obtain exact results with this degree of dilution requires very great care: it appears, therefore, that a solution, to be accurately titrated by the direct process, must be stronger than that employed in this experiment. These three experiments serve to show, that up to this limit the conversion into ammonia is as rapid and the results as accurate as with the stronger solutions employed in the preceding experiments. The nitrates in natural waters are seldom less than this limiting amount, so that the process will be found capable of extensive application without the necessity for reverting to distillation to concentrate the ammonia.

The estimation of the nitric acid in a natural water by this method is conducted in the following manner:—Some strips of zinc-foil or very thin sheet-zinc are placed in a wide-mouthed stoppered bottle and covered with a 3 per cent. solution of copper sulphate. When the zinc has acquired a sufficient coating of copper, the solution is poured off and the copper-coated zinc washed free from zinc sulphate and drained. A portion of the water to be analysed is then poured in and the couple rinsed with it, in order to displace the adhering distilled water. The couple is again drained, and finally the bottle is filled with the water to be analysed, the stopper inserted, and the

whole allowed to digest in a warm place until the reduction of the nitrates is completed. The water may then be found turbid with floating particles of oxide of zinc; to remove these, it is poured off the couple into a stoppered bottle and left at rest until the turbidity has subsided. A measured portion of the clear supernatant fluid is then withdrawn with a pipette, diluted to the necessary extent, and the ammonia in it titrated by Nessler's method.

The quantity of couple used for the analysis should be greater in proportion to the volume of the water than that employed in the above-described experiments. In these the reduction was purposely prolonged by employing a limited surface of zinc in order to facilitate the examination of the intermediate stages of the reaction. About 1 square decimeter of zinc (exposing a surface of 2 square decimeters) should be used for every 200 c.c. of a water containing 5 parts or less of NO_3 in 100,000. When the water is richer in nitrates a larger surface should be taken. A few words on the making of the couple may not be out of place here, because it is found that differences in the amount and condition of the deposited copper cause considerable variation in its activity. A copious deposit gives the most active couple ;* but if the deposition be pushed too far the copper is so easily detached that the couple cannot be washed without impairing its activity. The greatest care should be taken to insure a firmly adherent deposit, and this may readily be obtained by using clean zinc and a sufficiently dilute solution of copper sulphate (3 per cent. of crystallised salt is the best strength). Zinc-foil is usually greasy when received from the rolling mill, and should be washed with dilute alkali and then with faintly acidulated water before being made into "couple." The temperature of the copper solution and the presence of zinc sulphate have some influence upon the character of the deposit: a cold solution and the presence of a certain amount of zinc sulphate, appear to give the most firmly adherent deposits.

When it is desired to accomplish the analysis in as short a time as possible, the temperature must not be allowed to fall too low during the reduction. Experiment I shows how slowly the reaction proceeds when the solution is quite cold. The temperature of 24° adopted in the experiments will be found very convenient, and easily attainable in a warm place near a fire. Experience has shown that there is no appreciable loss of ammonia at this temperature when the operation is conducted in the manner described, even though the digestion be very prolonged. When stoppered bottles are employed and quite filled with

* These remarks apply only to the *wet* couple. The dry couple should be carefully distinguished from the wet, because the former is not at all adapted to hydrogenisations. The dry couple is very inefficient for the evolution of hydrogen, and has given very disappointing results when mistakenly applied to that purpose.

the water under analysis, the temperature may be raised to 30 or even 40° without fear, should occasion require the analysis to be made very quickly. Little or no hydrogen gas is evolved until the reduction is completed, so that no pressure of gas is developed in the bottles.

Experiments III and VIII indicate two additional means of expediting the reaction without interfering with the direct titration of the ammonia. It is easy to partially saturate a water with carbonic acid, or to add a fragment of salt (which must be quite free from ammonia) so as to make the reaction proceed to completion in a few hours. It may possibly be found that boric or oxalic acid, or any other acid that would not dissolve zinc, or otherwise interfere with the Nessler titration, might be substituted with advantage for carbonic acid or salt; but I have not made any exact experiments with these acids. If oxalic acid be found not to form any insoluble ammoniacal compound with the zinc, it will be admirably adapted to the purpose, because it will precipitate the lime from calcareous waters, and prevent it from interfering with the Nessler titration. It is found necessary to use rather more Nessler reagent than usual in titrating a water to which carbonic or any other acid has been added.

When operating upon an unknown specimen of water for the first time, the analyst will not know how long it may take to reduce all the nitrates. In such a case nitrous acid should always be tested for, before proceeding to estimate the ammonia. The test may most readily be made by adding metaphenylenediamine and dilute sulphuric acid to 25 or 50 c.c. of the water withdrawn from the couple. If, after half an hour, any trace of yellow coloration be found, the water should be allowed to digest upon the couple for a longer time. In this way it can be made certain that the reaction is complete, for it is found that the nitrous acid does not disappear completely until the whole of the nitrates have been converted into ammonia.

A little difficulty is experienced in treating calcareous waters by this process, because they sometimes become turbid when the Nessler reagent is added. Many waters that originally give a turbidity with this reagent, no longer do so when they have been digested upon the couple for a sufficient time. When a turbidity is still produced, a small fragment of pure oxalic acid should be added to the water poured off the couple, and when the calcium oxalate has subsided, the supernatant fluid may in most cases be titrated directly without further trouble. Permanent hardness in a water, when due to lime, does not interfere with the Nessler titration: a solution of ammonia in distilled water one-fifth saturated with calcium sulphate can be directly titrated without any turbidity being produced.

This process may thus be used for the majority of ordinary waters; for those which are coloured and those which contain magnesium or

other substances sufficient to interfere with Nessler's reagent, a portion of the fluid poured off the couple should be put into a small retort and distilled with a little sodium carbonate or pure lime, and the titration of the ammonia performed upon the distillates.

In calculating the amount of nitric acid existing in a water from the amount of ammonia given by this process of analysis, deductions must of course be made for the ammonia pre-existing in the water, as well as for that derived from any nitrous acid it contains. The nitrous acid may be estimated with great accuracy by Griess's meta-phenylenediamine process.

XXI.—*On the Absorption of Solar Rays by Atmospheric Ozone.*

By W. N. Hartley, F.R.S.E., &c., Professor of Chemistry, Royal College of Science for Ireland, Dublin.

Part I.

In his paper "On the Photographic Transparency of Various Bodies, &c." (*Phil. Trans.*, Part I, 1863), the late Dr. W. A. Miller remarks that the length of the solar spectrum is exceeded by the length of metallic spectra in the ultra-violet region. I have been led to attribute the limited extent of the solar spectrum, as photographed in London, to the selective absorption of rays by the tarry matters in the smoke of the town's atmosphere, especially since my experience of the extraordinary absorptive powers of benzene derivatives (*Phil. Trans.*, Part I, 1879). The effect of dust is distinctly different; carbon or other opaque matter in a finely divided state in the air would intercept the rays to some extent, but the effect would be a weakening of the whole spectrum, and this could be overcome by a longer exposure of the photographic plate. I have experienced this over and over again in photographing the absorption-spectra of turbid solutions. When, however, a minute quantity of such a substance as benzene or naphthalene is interposed between the rays and the photographic plate, the effect is very different, a portion of the spectrum being sharply cut off, or cut out, as the case may be, according to the nature and quantity of substance, and no increase in the period of exposure would supply the missing rays.

In like manner no reasonable amount of exposure will suffice to lengthen the sun's spectrum as it appears on a photographic plate. An instrument which was constructed for me nearly two years since,

was designed for the purpose of making observations on the sun's spectrum at different hours of the day, and under different meteorological conditions of the atmosphere.

During the year 1879, M. Cornu investigated the matter very completely (*Compt. rend.*, **88**, 1102). He observed that the atmosphere exerts an energetic absorption on radiations of short wave-length. The limit of the spectrum is variable, according to the state of the atmosphere and the altitude of the sun, which proves that atmospheric absorption determines the limit of the solar spectrum. The spectrum of iron in the voltaic arc yields rays identical with those in the sun (*Annales de l'Ecole Normale*, 1880), identical in position, and proportionately brilliant as the solar lines are dark. The solar spectrum extends only to $\lambda = 293$ millionths of a millimeter, while the iron spectrum extends to $\lambda = 200$. It was found that the extreme rays derived from electric sparks passed between electrodes of aluminium were absorbed by a stratum of air 1 meter in thickness.

These extreme rays of aluminium were described by Professor Stokes, in his paper "On the Long Spectrum of Electric Light" (*Phil. Trans.*, Part I, 1863), but neither Professor Huntington, when working with me, nor myself, was able to see or photograph them. The cause of this is not far to seek, the apparatus employed being fitted with lenses possessing an exceptional focal length of 3 feet, it follows that these rays were absorbed by the 6 feet of air in the collimator tube and camera. M. Cornu has photographed the sun's spectrum at different elevations up to 6,000 feet, on the Riffel, on the Rigi, and lower down at Viége (*Compt. rend.*, **89**, 808, 1879). The result of these observations showed that the longest spectrum was obtained near noon, at the highest elevation. The limit of the ultra-violet rays varies with the altitude only in a very feeble degree. The rate of progression is, however, in conformity with a theoretical value, which was deduced from the hypothesis of the atmosphere being a homogeneous absorbing medium.

The extraordinary absorption of the ultra-violet rays by ozone, and the proved existence of this substance as a normal constituent of the atmosphere, besides the vast extent of the atmosphere itself, is sufficient to cause one to consider whether the limitation of the solar spectrum may not be due to ozone. Experience in photographing the spectra transmitted by a large number of substances, chiefly benzene derivatives, which absorb the ultra-violet rays with great energy, has led me to observe that the effect of thickness of the layer of absorbent matter is practically *nil*, after a certain maximum effect has been produced, and that in substances exhibiting *absorption-bands* the maximum effect is reached soon after the absorption has become continuous, that is to say, when the second group of transmitted rays has become

extinguished. Under such circumstances, in judging of the absorption-spectrum of ozone, I am led to believe that nearly the maximum effect is produced when all rays are absorbed with a wave-length less than 293 millionths of a millimeter, and that the larger additions of ozone would only slightly increase the range of absorption.

We may reasonably suppose that the atmospheric ozone, even if immeasurably greater in quantity in the layer of the atmosphere through which we observe the sun, would not shorten the spectrum much more than the highly charged layer of oxygen only 3 feet in thickness, used in the preceding experiments.

The extreme limits of the solar spectrum transmitted by the atmosphere, as observed by M. Cornu, under the most favourable conditions, are the following:—

1879.	λ.	Altitude.
July 24th, Riffel	293·2	2570 meters
August 1st, Rigi	294·8	1650 „
July 28th, Viége	295·4	660 „

The shortening of the spectrum takes place at the rate of one millionth of a millimeter for the wave-length of the most refracted ray for each 900 feet of altitude. At later hours of the day, and at a lower level, a much greater stratum of air being traversed by the sun's rays, the extreme ranges photographed are described as follows:—

	True time. h. m.	Riffel.	True time. h. m.	Viége.
July 25th ..	5 43 P.M.	λ = 303·1	5 3 P.M.	λ = 302·0
„ ..	6 7 „	λ = 305·7	5 32 „	λ = 304·1

Hence it is evident, considering the small increase in absorbent action produced by so greatly an increased stratum of air, that the maximum absorptive effect of the normal atmosphere has been almost reached. If we were quite sure that oxygen and nitrogen were perfectly diactinic in layers of great thickness, there would be only one conclusion to be drawn from these facts, namely, that the absorbent constituent of the atmosphere is ozone, since the limit of the sun's spectrum corresponds with the limit of the absorption caused by this substance. It is possible that the absorption of solar rays is not entirely confined to the ultra-violet portion of the spectrum. I have shown that columns of air only 3 feet in length, containing only $\frac{1}{2000}$ of their volume of ozone, cause a most energetic absorption of the invisible rays, and I have now to make the statement that very small quantities of this gas give an azure-blue tint to very considerable volumes of air.

Messrs. Hautefeuille and Chappuis discovered the fact that the

ozone possessed a blue colour. On filling a glass tube 2 feet in length for the purpose of some of the preceding experiments, I was surprised to find how small a proportion of ozone is visible to the eye.

In a column of the atmosphere 1 square centimeter in sectional area, which would weigh 1033·33 grams (Roscoe and Schorlemmer, **1**, *Treatise on Chemistry*), the maximum amount of ozone would be at least 0·00258 gram, supposing the gaseous constituents of the atmosphere to form a homogeneous mixture. This calculation is based on the determination of the amount of ozone in the air made by M. Houzeau. The proportion by weight at the *maximum* was $\frac{1}{450000}$, or by volume $\frac{1}{700000}$ (*Compt. rend.*, **74**, 712—715). In a 2-foot tube a full pure sky-blue tint is seen when 0·002542 gram of ozone is contained in each square centimeter of sectional area. This number approximates very closely to the above, hence it is evident that if these determinations be correct, the blue tint of the atmosphere must certainly be due to some extent to ozone, at times if not always.

There are three circumstances under which a blue colour appears in a landscape. The sky is blue, the shadows are blue, and the distance is blue. Regarding the blue of the sky Professor Tyndall remarks that the idea that this tint was caused by minute particles floating in the upper atmosphere, "rendering the atmosphere a turbid medium through which we look at the darkness of space," is as old as the time of Leonardo da Vinci, or about four centuries since ("On the Blue Colour of the Sky, the Polarisation of Sky-light, and on the Polarisation of Light by Cloudy Matter Generally" (*Proc. Roy. Soc.*, 1869). These experiments prove most distinctly that light is reflected from the heavens during a cloudless day. It is supposed that this light is blue, because the particles are so minute that they reflect chiefly the blue rays or those of smallest wave-length. Many such effects are well known to be produced from finely divided matter. But what I wish to point out is, that if ozone exists in the higher regions of the atmosphere, even white light, such as would be reflected from white fleecy clouds at great elevations, must appear blue, since our view of them is through a blue gas. On gazing intently at the blue sky on a day of cloudless sunshine, there is invariably to be seen a faintly mottled appearance, the sky is not of one uniform blue tint, there are parts here and there innumerable where the blue tint is more opaque, one can hardly say lighter in colour, but of a less transparent hue, and this appearance will remain for hours and hours unchanged. It may be a thin layer of white fleecy cloud, through which is seen the deeper blue beyond; but if this be the case, and the amount of ozone in the atmosphere is sufficient to make the atmosphere actually blue, these filmy clouds must appear bluer than they are in reality, and the sky must everywhere exhibit a bluer tint than it would otherwise

possess. Of course the interposition of a blue medium would not affect the phenomena of polarisation in any degree.

The blue of shadows is undoubtedly caused by the illumination of the shaded portion of a landscape, by reflection from the sky overhead. I believe the first to explain this was Mr. John Brett, and the application of this scientific principle in his hands has produced the most brilliant effects in landscape painting. If we consider now the effect of distance when the air is clear, as for instance, during a brisk south-west breeze, on viewing a mountainous coast from a vessel at sea, the richest and deepest blue tints are those of the far horizon. In such a case it is impossible to believe that a stratum of air in any thickness from 5 to 50 miles, when charged with ozone at the maximum, is not a blue medium through which the distance is seen. Were haze, or let us say floating particles, the cause, the greater thickness of the layer would lend a greater degree of opacity to the blue. I am not so much referring to the depth of tint as to the transparency. There are indeed two distinct kinds of blue distance, and during the past summer, I have been much engaged in observing the character of the tints under varying conditions. On one occasion, I observed from the entrance to the Sound of Mull, the whole range of mountains stretching from Ben Cruachan to Ben Nevis in as clear an atmosphere as it is possible to see. The horizon was bathed in the purest and most transparent blue, the outlines of hills and rocks being perfectly distinct and sharp, the shadows being of an intense deep tint, and the most distant objects the deepest in colour. This is not generally the effect produced by a turbid medium. The distances in this case ranged from 27 to 35 miles.

On another occasion I viewed the mountains in Skye from the coast of Rum, at a distance of 12 or 15 miles. Overhead and around was blue sky with exceedingly filmy clouds, not visible at the first glance; the horizon was a pure blue, but opaque in character; there was a want of that depth of shadow and sharpness of outline seen in the former case. I have no doubt that the difference was caused in the latter case by the greater amount of floating matter in the air.

Now, if we consider that 2·5 mgrms. of ozone in each square centimeter of sectional area of a column of air produce a full sky-blue tint, it is impossible to believe that light, which has traversed columns of air under ordinary conditions of temperature and pressure, and 27 to 35 miles in length, has not made its way through 2·5 mgrms. of ozone. The length of an atmospheric column at the ordinary temperature and pressure would be $5\frac{1}{4}$ miles, and while we are in doubt as to the constitution of the higher atmosphere, such reasoning cannot justly be applied to the blue colour of the sky.

I will now proceed to show proof of the diactinic character of the

various minute constituents of the earth's atmosphere other than ozone.

I have availed myself of the records of the Meteorological Observatory of Montsouris, published in the *Annuaires* for 1878 and 1879.

The weight w of a substance in the atmosphere which could possibly cause absorption of the sun's rays at noon-day is found by the simple calculation—

$$w = \frac{w'}{124{,}450} \times 1033{\cdot}33$$

where w' = the ascertained weight in grams of the substance per 100,000 litres of air.

1033·33 = the weight in grams of a vertical column of air 1 square centimeter in sectional area, or the barometric pressure expressed in grams and centimeters.

124,450 = the weight in grams of 100,000 litres of air at T = 10·7° C. and bar. = 760 mm.

10·7° C. = the mean temperature of the year ending September, 1879.

In the case of aqueous vapour the mean tension for the year 1878–79 was 7·53 mm., the mean barometric pressure being 752 mm., hence the water vapour in the atmospheric column was

$$\underset{\text{mm.}}{\frac{7{\cdot}53}{752}} \times 1033{\cdot}33 = \underset{\text{grams.}}{10{\cdot}34}$$

The average amounts of ozone and ammonia in the year 1878–79, and of oxides of nitrogen expressed as nitric acid in 1876–77, have been taken from the Montsouris *Annuaires*.

The amount of hydrogen peroxide is the maximum taken from Schœne's researches (*Ber.*, **7**, 1698—1708).

	w'.	w.	Proportion by weight of an atmosphere.
Ozone.....	0·00097	0·0000083	$\frac{1}{124450000}$
Ammonia	0·002	0·0000166	$\frac{1}{62225000}$
Oxides of nitrogen	0·003	0·0000252	$\frac{1}{41000000}$
Peroxide of hydrogen	0·0004	0·0000033	$\frac{1}{320000000}$

Carbonic acid, as determined at Montsouris, is stated in litres, thus for eleven months in the year 1878–79 the average amount was 35·4 litres of CO_2 per 100,000 of air. As the specific gravity of carbonic acid compared with air is 1·5241, the proportion by weight is 22·6 parts per 100,000.

$$\text{then } w = \frac{22{\cdot}6}{100{,}000} \times 1033{\cdot}33 = 0{\cdot}2335 \text{ gram } CO_2.$$

I will now take into consideration the diactinic quality of the various constituents of the atmosphere *seriatim* in columns 1 square centimeter in section.

Water = 10·34 grams; this is perfectly diactinic, indeed as much as 60 centimeters show no signs of absorption. This is directly contradictory to the statement of J. L. Schönn (*Wiedemann's Annalen*, 1880, **9**, 492), but I have no hesitation in saying that Schönn must by accident have got some impurity into the water he examined, since, though he states that a layer of water 10 cm. in thickness absorbs a great part of the ultra-violet rays, yet a block of ice 21 cm. in thickness transmits all the lines of cadmium. Now it has been proved by the late Dr. W. A. Miller, and his experiments have over and over again been confirmed by myself, that when a substance in the solid state is diactinic, it possesses this property when liquefied or when converted into vapour.

Ozone.—According to the Montsouris observations, this would amount to 0·0000083 gram. This number cannot be regarded as being equal to the average amount of ozone in the air, I therefore reject it for reasons which will be fully given later on.

Ammonia = 0·0000166 gram. A solution of ammonia containing 50 volumes of the gas is perfectly diactinic in layers 15 mm. in thickness, that is to say 0·057 gram, or more than 3,000 times the above quantity.

The Oxides of Nitrogen.—Expressed as nitric acid these would amount to 0·0000252 gram.

Remarkable variations in the proportion of nitric acid in the air have been noticed. For instance, on the 21st and 22nd June, 1877, there appeared to be none; on the 23rd, after a storm, it reached the enormous quantity of 12 mgrms. per litre, or more than a million times the above average quantity during seven months. There are three points which serve to determine the fact that the oxides of nitrogen cannot play any part in the absorption of solar rays. 1st. They undoubtedly exist in the atmosphere as ammonia salts of nitric and nitrous acids, which in minute quantities are quite diactinic. 2nd. If present in sufficient quantity in the free state to absorb the visible rays, the colour of the sky would be any colour but blue. 3rd. I have had photographs taken of the spectrum transmitted by NO_2 and N_2O_3, and find that these gases absorb in a most extraordinary manner precisely those rays which are transmitted by ozone, and transmit those which ozone absorbs, or in other words, it is the portion of the sun's spectrum which reaches us which the oxides of nitrogen have most power to absorb. The accompanying diagram, prepared from photographs, shows the amount of absorption caused by 16·6 c.c. of nitric peroxide, prepared by heating lead nitrate. The gas evolved by the

action of starch on nitric acid, and of arsenic trioxide on nitric acid, was also photographed, and found to give the same spectrum as NO_2. It is well known that those gases are not pure N_2O_3, but mixtures of NO_2 and N_2O_3; in order, therefore, to separate any nitric acid which might pass over, and to absorb if possible the NO_2, the gas was washed with a strong solution of potassic nitrite. This washing was expected to effect the elimination of the NO_2, by first absorbing it in the usual way, by which it is split up into nitrous and nitric acids. The nitric acid would then liberate nitrous acid from the potassium salt. If, however, the nitrous acid formed were decomposed according to the equation—

$$2HNO_2 = H_2O + NO + NO_2,$$

then the gas NO would mingle with the air of the tube into which it was delivered, and yield NO_2.

Peroxide of Hydrogen = 0·0000033 gram at the maximum. Schœne has made very successful attempts to estimate peroxide of hydrogen in moisture condensed from the air. This he effects by liberating iodine from potassium iodide and measuring the coloration given to starch thereby. A solution of ozone in water would give the same reaction, and, according to Carius, 4 vols. of ozone dissolve in 1000 of water. Whether the substance obtained by Schœne be ozone or peroxide of hydrogen is of little moment, since a quantity of this substance, 1000 times as large as the above quantity, transmits all rays as far as $\lambda = 239{\cdot}0$.

Hydrogen peroxide exerts considerable absorptive power on the ultra-violet rays. A solution prepared by passing carbonic acid through barium peroxide suspended in water, was tested especially to ascertain the proportion of H_2O_2 it contained. The operation was carried out in the following manner:—The solution was acidulated with sulphuric acid and allowed to run into one of Dr. Frankland's nitric acid tubes standing over mercury; there was then mixed with it a strong solution of potassium permanganate. After shaking, oxygen soon begins to be evolved very briskly; the gas was then transferred to a graduated tube surrounded with water and exactly measured. The reaction which takes place is the following:—

$$2KMnO_4 + 3H_2SO_4 + H_2O_2 = K_2SO_4 + 2MnSO_4 + 3O_2 + 4H_2O.$$

(1.) Peroxide of hydrogen takes 2 c.c. oxygen measured = 14·8 c.c. Bar. 29·5 inch. T = 4° C.

(2.) Peroxide of hydrogen takes 1 c.c. oxygen measured = 7·6 c.c. Bar. 29·7 inch. T = 5° C.

Corrected for temperature and pressure—

(1.) 14·34 c.c. of oxygen = 0·0073 gram of H_2O_2
= 0·00365 H_2O_2 per c.c. of solution.

(2.) 7·38 c.c. of oxygen = 0·0037 gram of H_2O_2 per c.c. of solution.

5 c.c. of this solution, presenting a thickness of liquid equal to 15 mm., absorbed all the rays more refrangible than those with $\lambda =$ 292·5 millionths of a millimeter.

Carbonic Acid = 0·2335 gram. This quantity is equal to a layer of the gas 122·6 cm. in thickness at 0° C. and 760 mm. A layer of the gas 175 cm. in thickness at 6° C. and bar. 760 mm. is quite diactinic. The above quantity is therefore incapable of absorbing the sun's rays in the ultra-violet region.

From the foregoing experiments it is evident that the only minute constituent of the atmosphere capable of limiting the solar spectrum to such an extent as has been the subject of frequent observation is ozone.

It seems, however, to be desirable that some further knowledge should be gained on the following points before coming to a decision:—

1st. Are the methods adopted for estimating the quantity of ozone in the air strictly accurate?

2nd. Is ozone a constant constituent of the higher atmosphere, and, if so, in what proportion is it probably present?

3rd. What is the maximum absorptive effect of ozone in the ultra-violet rays?

4th. Is it possible for pure oxygen and nitrogen to absorb rays of such low refrangibility as $\lambda = 307·0$, even when a greater thickness of gas is traversed?

Part II.

I will now take the foregoing questions and discuss them in their order, and give details of the experiments upon which I have been more recently engaged, the execution of which has been carried out with great care by Mr. W. E. Adeney, Associate of the Royal College of Science.

On the Methods Employed for Estimating the Amount of Ozone in the Air.

M. Houzeau's Method.—Ozone test-papers such as are employed in examining the atmosphere are prepared in the following manner:—A solution of litmus is acidified by the addition of just so much sulphuric acid as is necessary to give it a permanent red tint, when a drop is evaporated on a plate of white porcelain by mere exposure to the air. If the drop should turn blue on drying, it is necessary to add a further quantity of acid. The strength of the solution is such

that when dried at 100° C. 1 c.c. will yield a residue weighing 0·012 gram. Unsized paper is steeped in this solution. When dry the strips of paper are impregnated for a fourth of their length in a solution containing 1 per cent. of neutral potassic iodide. These papers are insensitive to free oxygen, to the oxides of nitrogen, and likewise to such minute traces of hydrogen peroxide as are found in the atmosphere. They acquire an evanescent blue colour by exposure to 0·0002 mgrm. of ozone, and this is the limit of their sensitiveness. They change colour rapidly when placed in moist air containing $\frac{1}{261000}$ of its weight of ozone. The oxidation of the potassic iodide yields iodine and free potash, which blues the reddened litmus. By comparing the action of the atmosphere on ozone papers with that of 12 litres of air saturated with moisture at 14° C. and containing 0·057 mgrm. of ozone, it was found that the air never contains as much as $\frac{1}{261000}$ its weight of this substance. The maximum quantity was estimated to be about $\frac{1}{450000}$ by weight, or 1 volume in 700,000 of air.

Method of P. Thénard.—The process depends upon the oxidising action of ozone on arsenious acid; it affords a means of determining the amount of ozone in air at once more simple, more rapid, and more accurate than that of Houzeau. The unoxidised arsenious acid is titrated with potassic permanganate.

An equal volume of nitric acid containing 50 per cent. of HNO_3 has no action on the solution of arsenious acid. Nitric peroxide reduces the permanganate solution, so that should it gain access to the arsenious acid solution it would lower the figures representing the proportion of ozone. The same effect would result from the presence of hydrogen peroxide, since it does *not oxidise* the arsenious acid, but it does reduce the permanganate. It was proved that oxygen ceased to affect the arsenious acid as soon as the ozone had been withdrawn. As M. Thénard mentions, on account of the above facts the process has only one fault, and that is, the numbers obtained represent *minimum* and not *maximum* quantities, and this is a point of great importance. The arsenious acid solution is made by dissolving the solid substance in hydrochloric acid, and diluting to such an extent that 1 c.c. of the solution is equivalent to 1 mgrm. of oxygen. After 10 c.c. or 20 c.c. of the solution have been exposed in the flask containing the ozonised air, the liquid being shaken up repeatedly and allowed to stand, 30 c.c. of sulphuric acid are added containing 1 per cent. H_2SO_4, and titration is effected in the usual manner with permanganate.

Method of M. Lévy.—The following process is in use at Montsouris, where the ozone is collected during 24 hours daily and quantity estimated. The air is aspirated by a water jet with eight-fall tubes

and submitted to the action of 20 c.c. of distilled water, 2 c.c. of arsenite of potash containing 0·730 gram of the salt per litre, 1 c.c. of potassic iodide free from iodate. The arsenite of potash is oxidised to arsenate, the change being facilitated by potassic iodide. Previous to estimating the unchanged arsenite, about 20 drops of a saturated solution of carbonate of ammonia are added, and 1 c.c. of starch-paste containing 1 per cent. of starch. The estimation is effected with very dilute iodine solution in the usual manner. As the strength of the potassic arsenite varies slightly by keeping, it is the custom to acidify it and to neutralise the acid just before use by adding a few drops of a solution of potassic bicarbonate.

I have adopted this method and found it most exact.

It must be conceded that the observations as carried out at the Observatory of Montsouris are models of accurate work so far as the estimation of the substances *collected* in the absorbent liquids is concerned; but the experience of Dr. Angus Smith has shown that there is a great difficulty in absorbing the minute constituents of the atmosphere by passing large volumes of air through liquid reagents, even when the greatest care is taken to keep the liquid in a state of agitation and in contact with every particle of the gas. No experiments of the kind have been completely successful even when the tubes which deliver the air into the liquid are made in the form of a rose. ("The Examination of Air," R. Angus Smith, Ph.D., F.R.S., *Proc. Roy. Soc.*, **26**, 512, 1877.) The collection of ozone by means of aspiration through tubes is especially difficult, since the air has to pass through a plug of cotton-wool or asbestos in order to stop soot and dust or rain. This soot or organic dust which the air must come in contact with, would certainly lead to the destruction of the ozone to a great extent. Moreover, it has been shown by Professor Palmieri, of Naples, that if ozone be passed through glass tubes it is destroyed, an effect, no doubt, caused by the adhesion of dust to the walls of the tubes.

The same fact was noticed by M. Houzeau (*Compt. rend.*, **74**, 1266). It is impossible, therefore, to accept the figures given in the *Annuaire de l'Observatoire de Montsouris* as indicating anything like the true proportion of ozone usually present in country air, but they give useful comparisons.

I am inclined to believe that M. Houzeau's experiments may be relied on as giving us a close approximation of the amount of ozone when at the maximum in the lower regions of the atmosphere, and for the following reason. The odour of ozone in country air has been noticed by Houzeau, Chevreul, Boussingault, and Würtz. It has been remarked that linen hung out exposed for 12 hours to country air acquires a smell of dilute ozone, while it is known that such fabrics can condense ozone to such an extent as to possess the characteristic

smell. Now the odour of ozone is a thing quite unique; there is certainly nothing like it to be found in nature, and I have therefore thought it worth while to estimate the smallest portions of ozone that can be detected by the sense of smell.

Ozonized air containing 0·0018 gram per litre of ozone was delivered in accurately measured volumes into a large glass jar holding nearly 15 litres. The jar was carefully covered with a glass plate, and the gases were allowed to mix by diffusion. After a sufficient time had elapsed the mixture was smelt by putting the face quite into the jar and inspiring the gas rapidly. 10 c.c. of the ozonised air gave a very distinct odour, quite unmistakeable, but quite reminding one of the air on the South Downs during a south-west breeze, or on the moors of North Britain. 7 c.c. had the usual smell of fresh air; 5 c.c. had no odour.

Taking 7 c.c. as the limit—

$$\frac{7 \times 0{\cdot}0018}{1000} \text{ gram} = 0{\cdot}0000126 \text{ gram ozone.}$$
$$= 0{\cdot}00586 \text{ c.c. ozone in 15 litres.}$$

The proportion of ozone perceptible to the sense of smell, and quite commonly present in fresh air, I conclude to be—

1 in 1,470,000 parts by weight.
1 in 2,500,000 parts by volume.

On high land, where there is but little vegetation, and during breezy weather—

1 in 1,870,000 parts by volume.

There is this peculiarity about the odour of minute quantities of ozone, that one may discriminate very nicely between two mixtures containing different proportions of the gas up to a certain point, after which considerable variations in strength cannot be detected.

Is Ozone a Normal Constituent of the Higher Atmosphere?

The conclusion that ozone, like carbonic acid, is a normal constituent of the atmosphere was derived from a series of experiments made by M. Jules Reiset at Ecorchebœuf, which confirmed a similar set of experiments conducted elsewhere by M. Houzeau. The intensity with which it acts, however, at any given spot is often variable, the quantity being notably larger at higher elevations than near the surface of the soil. The direction of the wind and the lowness of the temperature cause much larger quantities of ozone to pass over certain localities at particular periods than can be represented by yearly averages, or even by the maximum quantity collected in 24 hours. If

it were possible to estimate the hourly variations, I believe it would be found that air very rich in ozone occasionally sweeps over the country for short intervals. A most interesting diagram appears in Montsouris *Annuaire* for 1876–77, showing the variations of the ozone and ammonia in the air, accompanied by variations in the wind. The maximum quantities of both these substances prevail

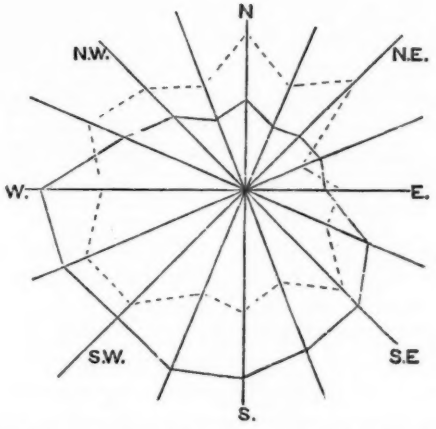


DIAGRAM SHOWING THE INCREASE OF AMMONIA AND OZONE WITH THE PREVALENCE OF W. AND S.W. WINDS. (From the Montsouris *Annuaire*.)

when the wind blows from the south-west and west-south-west. A line drawn from north-west to south-east divides the whole quantity into a maximum and a minimum. This is a most significant fact. It proves in the first place that ozone and ammonia can exist together without reacting to produce ammonium salts of nitrous or nitric acid as suggested by Carius (*Liebig's Annalen*, **174**, 31—35; see also *Chem. Soc. J.*, 1875, 128). Whatever chemical action may take place with strong ammonia, it is evident that when the gases are reduced to a very small tension they are neutral. Secondly, we have a most distinct proof here that both gases are normal constituents of the higher atmosphere in much larger proportion than near the earth's surface. A little consideration of the origin of the south-west and west-south-west winds will make this evident. They are air-currents travelling from the equator towards the poles, which have been cooled sufficiently to drop from the heavens in these latitudes. I consider that we have here quite sufficient evidence for believing that the blue of the sky, even much more than the blue of distance, is due in no inconsiderable degree to ozone.*

* Since the above was written, this conclusion has been confirmed, for M.

On the Maximum Actinic Absorption exerted by Ozone.

Renewing the experiments on the absorption of the ultra-violet rays by ozone necessitated a disjointing of the apparatus previously used. The potash-purifier designed to take any trace of oxides of nitrogen out of the ozone was found to contain a yellow substance which thickly coated the sticks of potash placed on the top of pumice. On dissolving this in water and acidifying with sulphuric acid, the reactions of hydrogen peroxide were obtained with the solution: it liberated iodine from iodide of potassium; it decolorised permanganate of potash. Hence, contrary to the statement that ozone has very little action on potash (*Watts's Dictionary*, **4**, 302), it is absorbed by that alkali with ease, the product being apparently potassium peroxide, though the quantity of substance obtained was not sufficient to enable us to establish its composition.

It has been shown that the action of the oxides of nitrogen on the ultra-violet rays differs in a very marked manner from that of ozone, and as their presence could easily be detected by the appearance of the spectrum photographs, this potash bottle was removed to a position behind the ozoniser to purify the oxygen previous to drying it. Increased certainty in drying the oxygen was attained by the addition of a bottle containing phosphorus pentoxide to the oil of vitriol apparatus. Means were taken to prevent the phosphoric anhydride being blown over into the connecting tubes, by interposing a second bottle of sulphuric acid.

The ozone tube of M. Houzeau was tried. This is certainly the simplest and one of the most effective forms of apparatus. Eventually the tube made use of by Sir Benjamin Brodie (*Phil. Trans.*, 1872, vol. **162**, p. 438) was employed. It is usually figured in French books as the apparatus of M. Berthelot. Instead of charging the ozone tube with acidified water inside and out, a freezing mixture of ice and salt was used as the conducting medium. So prepared with previously cooled oxygen, the yield of ozone was very satisfactory.

The method of procedure in taking photographs of various thicknesses of ozone and estimating the tension of the gas in the oxygen was the following:—

A reservoir of oxygen was connected with the purifying and drying

Chappuis has established the fact that three bands in the visible spectrum of ozone correspond with certain atmospheric bands in Ångström's chart.

"The relative stability of ozone at low temperatures and pressures, and the almost incessant production of this body by electric discharges make it an important element in the higher regions of the atmosphere; its blue colour certainly plays an important part in the colour of the sky" (Chappuis, *Compt. rend.*, **91**, 986).—W. N. H., January 12th, 1881.

apparatus. From the ozoniser a **T**-tube with glass stop-cocks on it communicated with the brass tubes to be filled with ozone, and likewise with a glass gas-holder charged with purified oil of vitriol, and capable of holding 5 or 6 litres of ozone. One of the tubes, fitted at each end with plates of quartz, was 6 feet in length and $1\frac{1}{2}$ inch in diameter, the caps securing the quartz plates were luted on with melted paraffin. Side tubes 3 inches in length and $\frac{1}{4}$ inch diameter placed at each end, served as an entrance and exit for the gas. The collimator tube was made use of as in the previous experiments. This being 3 feet in length, it was easy to photograph layers of gas 3, 6, and 9 feet in thickness. When the tubes were charged the gas-holder was filled. After the photographs were taken, the ozone in the sample of gas contained in the gas-holder was estimated. All the junctions of the different tubes were either fused glass, paraffin lutings, or made with corks well soaked in melted paraffin. In making the analyses, the following solutions were used:—(1.) Arsenious acid dissolved in sodic carbonate, the strength being double that of a decinormal solution, that is to say, there were 198 parts As_2O_3 in 14,000 of water. (2.) Potassic iodide solution completely freed from traces of iodate by repeated evaporation to dryness after treatment with hydrochloric acid. (3.) Solution of iodine in potassic iodide, each cubic centimeter containing 0·00636 gram of free iodine, equivalent to 0·0012 gram of ozone. A solution of starch of course was used as the indicator. In making an estimation of the ozone, 5 c.c. or 10 c.c. of the arsenious acid solution were mixed in a stoppered cylinder holding 500 c.c., with 2 c.c. of the potassic iodide and about 200 c.c. of water. An accurately measured volume, 200 or 300 c.c., of ozone from the gas-holder, were allowed to bubble slowly through the liquid, the stopper was then replaced, and the contents of the cylinder were well shaken. With each set of analyses blank experiments were made with the arsenious and other solutions. Previous to titrating, the liquids were acidified with hydrochloric acid to destroy any iodate that might possibly be formed by the ozone, the liquids being neutralised again with bicarbonate of soda. The strength of the ozone photographed in columns 9, 6, and 3 feet long, is shown by the following figures:—

Arsenious acid solution used = 10 c.c.
Iodine solution used = 56·7 c.c.
Ozonised oxygen = 200 c.c. at 6° C. and 748·4 mm. barometric pressure.

A blank experiment with the same quantity of each of the different solutions required 58·4 c.c. of iodine to produce the same tint of blueness with the starch solution:—

58·4 c.c. − 56·7 c.c. = 1·7 c.c.
1·7 „ × 0·0012 gram = 0·00204 gram ozone in 200 c.c. of the gas = 0·0102 gram per litre.

A litre of oxygen at 6° C. and 748·4 mm. pressure = 1·381 gram; therefore 0·0102 gram of ozone in 1·381 gram of oxygen = 1 part of ozone in 135·4 of oxygen = 0·7337 per cent., or 1·1 volume per 100.

The tubes hitherto mentioned as 3 feet and 6 feet in length actually measured 92 cm. and 196·5 cm. respectively. The terminations of the photographs of spectra transmitted through those tubes, when filled with ozonised oxygen, were as follows:—

Extreme ray transmitted.	Length of column of ozone and oxygen.	Actual volume of ozone in columns 1 sq. cm. in sectional area.
$\lambda = 303{\cdot}5$ in	92 cm.	1·012 cm.
$\lambda = 315{\cdot}0$ in	196·5 cm.	2·162 „
$\lambda = 316{\cdot}0$ in	288·5 „	3·175 „

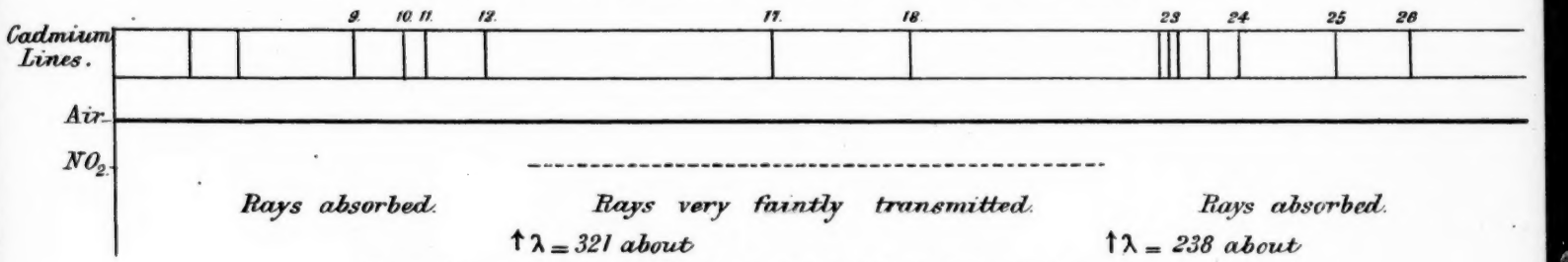
It is evident from these figures that the extreme rays, capable of absorption by considerable quantities of ozone, is about $\lambda = 316$, since there is but little difference between the absorption in the 6 and the 9-foot tubes. A second series of photographs was taken from a fresh supply of ozone:—

Ozonised oxygen at 6° C., and 748·4 mm.
Barometric pressure = 300 c.c.
Arsenious acid solution = 5 „
Iodine solution used = 27·6 „
Blank experiment required = 28·9 „ and 29·0 c.c.
28·9 c.c. − 27·6 c.c. = 1·3 c.c. iodine solution.
1·3 „ × 0·0012 „ = 0·00156 gram ozone.
= 0·0052 gram per litre.
= 1 part of ozone in 265·6 parts of oxygen.

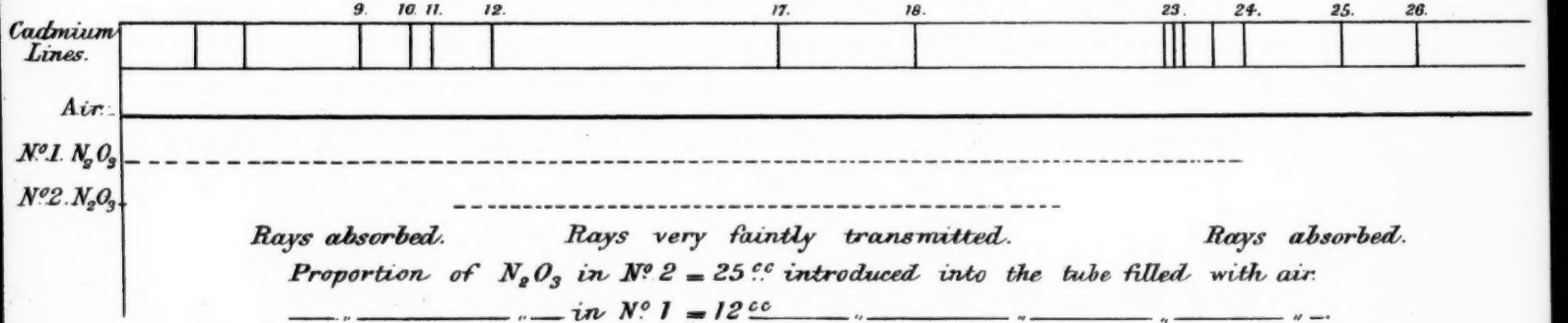
Although in the latter case the quantity of ozone was double that examined in the former, yet the absorption caused in the 9-foot column appeared no greater. On another occasion the 92-cm. tube was filled with gas containing as much as 0·13872 gram of ozone per litre. It yielded the same absorption spectrum, although the quantity of ozone was 27 times as great as in the previous case. There can be no doubt about this being the *maximum* effect producible by ozone.

The method of ascertaining the wave-length of the most extreme rays is only a rough one. The cadmium lines of known wave-lengths are drawn from photographs on a sheet of Waterlow's sectional paper divided into one-twentieths of an inch. Diagonals are drawn from the

SPECTRA TRANSMITTED BY OXIDES OF NITROGEN.


Cadmium Lines.
9. 10. 11. 12. 17. 18. 23 24 25 26
Air.
NO_2.
Rays absorbed. Rays very faintly transmitted. Rays absorbed.
↑λ = 321 about
↑λ = 238 about

Proportion of air 800 cc in a tube 36 inches in length.
Proportion of NO_2 16·6 cc introduced into the tube filled with air.


Cadmium Lines.
9. 10. 11. 12. 17. 18. 23. 24. 25. 26.
Air.
№1. N_2O_3
№2. N_2O_3
Rays absorbed. Rays very faintly transmitted. Rays absorbed.
↑λ = 336 about.
λ = ↑237 about
↑λ = 224 about.

Proportion of N_2O_3 in № 2 = 25 cc introduced into the tube filled with air.
" " " in № 1 = 12 cc " " " " "

Harrison & Sons, Lith. St Martins Lane, W.C.

extremity of one line to the further extremity of the next, and these diagonal lines are divided into as many divisions as there are millionths of a millimeter in wave-length between the two cadmium lines. All one has to do in measuring the wave-length of a ray is to apply the photograph to the diagram in such a way that a particular air-line at the least refrangible end corresponds with that in the diagram, and run the plate down the paper until one of the diagonals touches the extremity of the spectrum. If the photographs were perfectly sharp and dense at the edges, that is to say, at the extremity, and the diagrams were perfectly correct, this method would be exceedingly convenient and very accurate.

The engraved lines on Waterlow's paper are by no means true, and the photographs become shaded off and exceedingly faint before the end of the spectrum is reached. I hope soon to get much more exact readings by photographing the absorption of the iron spectrum by ozone and comparing the effect of different quantities of ozone with the appearance of the sun's spectrum under varying atmospheric conditions.

The ozone with which a tube was filled, in order to observe the blue colour, was taken from a glass gas-holder:—

200 c.c. were taken for each analysis.
5 c.c. of arsenious acid,
1 „ of potassic iodide.

I. Iodine solution used = 22·5 c.c.
II. „ „ = 22·6 „
Blank experiment = 29·0 „

Taking the mean amount of iodine or 22·55 c.c. for the calculation—

29 c.c. − 22·55 c.c. = 6·45 c.c.
= 0·00774 gram of ozone.
= 0·0387 „ or 18 c.c. of ozone per litre.

In the 2-foot glass tube this gas appeared as blue as the sky on a brilliant day. Even the cross section of the tube showed a faint colour on white paper, which was rather more of a pale lilac than a blue tint. The depth of blueness is best seen by viewing the tube in such a way that pieces of white and yellow paper placed side by side are seen simultaneously. Bright turmeric paper was used for this purpose.

The foregoing experiments and considerations have led me to the following conclusions:—

1st. That ozone is a normal constituent of the higher atmosphere.

2nd. That it is in larger proportion there than near the earth's surface.

3rd. That the quantity of atmospheric ozone is quite sufficient to account for the limitation of the solar spectrum in the ultra-violet region, without taking into account the possible absorption caused by the great thickness of oxygen and nitrogen.

4th. That the blue tint of the atmosphere is due to ozone.

I am also entirely of opinion that a spectroscope-camera, such as I have been using, may become a valuable meteorological instrument, because the ultra-violet rays are so exceedingly sensitive to the absorptive action of very minute traces of substances, and notably to certain traces of ozone.

XXII.—*On the Synthetical Production of Ammonia by the Combination of Hydrogen and Nitrogen in presence of Heated Spongy Platinum* (Preliminary Notice).

By George Stillingfleet Johnson, King's College, London.

In the course of my experiments on the "Occlusion of Hydrogen by Copper," the results of which were published in this Journal in May, 1879, being anxious to ascertain whether hydrogenised copper is capable of retaining its occluded hydrogen when heated in a gas which has no chemical action upon it, I investigated the action of *nitrogen* gas at a red heat upon freshly hydrogenised copper, and found the occluded hydrogen was entirely lost by the metal under those conditions. Subsequently, advantage was taken of this fact in order to determine how far the water collected on heating recently hydrogenised copper in dry air was due to aqueous vapour or *moisture* retained by the reduced metal, and how far to the oxidation of occluded hydrogen gas. For this purpose, I passed a stream of dry pure nitrogen gas through a series of tubes, the first of which was a combustion-tube containing metallic copper recently reduced in hydrogen gas, the second being a counterpoised tube containing sulphuric acid, the third a hard glass tube containing oxide of copper, and the fourth a second counterpoised tube containing sulphuric acid. The oxide of copper-tube was heated to redness first, and the nitrogen passed till the second H_2SO_4-tube had a constant weight.

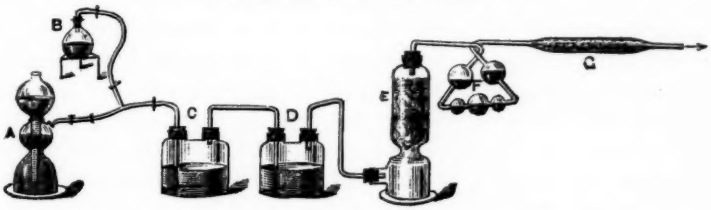
The hydrogenised copper was then heated in a stream of nitrogen, the CuO-tube being still kept at a red heat. In all cases the second H_2SO_4-tube gained weight due to water produced by oxidation in the CuO-tube of occluded hydrogen evolved by the copper at a red heat

in an atmosphere of nitrogen; but it was also noticed that a small quantity of white saline matter collected in front of the first H_2SO_4-tube, and this suggested the possibility of the formation of traces of *ammonia* by combination of nitrogen with a portion of the hydrogen evolved from the heated copper.

Acting upon this hypothesis, I passed a mixture of hydrogen and nitrogen gases, carefully purified, over spongy copper and over asbestos at a red heat, and obtained in both cases minute traces of ammonia; so small a quantity, in fact, that the results were not deemed worthy of publication at that time, though sufficiently suggestive to make it well worth while to attempt the synthesis of ammonia by such metals as *spongy platinum*, spongy palladium, &c.*

The opportunity long delayed, arrived a few days since, and I determined to investigate the action of spongy platinum upon a mixture of pure hydrogen and nitrogen gases at a low red heat. With this purpose in view, I fitted up the following apparatus:—

APPARATUS FOR THE PRODUCTION OF AMMONIA BY SYNTHESIS FROM NITROGEN AND HYDROGEN.



A contains zinc and sulphuric acid, from which hydrogen gas is evolved, and enters the Woulffe's bottle C, which contains a solution of nitrate of silver, next passes through D, which contains oil of vitriol, then through E, which contains fragments of pumice-stone moistened with oil of vitriol, then through the bulbs F, which contain "Nessler reagent," then through the tube G, which contains the spongy platinum. The spongy platinum having been heated to redness in pure hydrogen, and the absence of ammonia therein being proved by a negative result with the Nessler test, the solution of nitrite of ammonium in the flask B was heated until nitrogen gas was evolved, and, mixing with the hydrogen, passed through the drying and purifying apparatus, and came in contact with the heated spongy platinum.

* I was the more anxious to investigate this matter, as the only experiments I could find recorded bearing upon the subject were those of Professor Donkin, who succeeded in obtaining traces of ammonia by the action of induced electricity upon a mixture of nitrogen and hydrogen, but did not obtain quantities sufficient for gravimetric analysis.

As soon as the mixed nitrogen and hydrogen gases reached the hot spongy platinum *ammonia* was produced, as shown by the brown colour assumed by the Nessler reagent, by the odour of the gas as it issued from the tube, by the restoration of the blue colour to reddened litmus exposed to its action, by the fumes which it produced with vapour of hydrochloric acid, &c.

The experiment was repeated *ab initio* several times with the same platinum, and always with precisely similar results.

In two experiments pure nitrogen was passed over the heated platinum first, and, after all ammonia had been expelled, hydrogen was allowed to mix with the nitrogen, when the ammonia was at once reproduced as before.

Having thus proved *qualitatively* that ammonia is produced synthetically when a mixture of pure hydrogen and nitrogen gases is passed over heated spongy platinum, I made a *quantitative* experiment by collecting the ammonia produced in bulbs containing a known volume of standard sulphuric acid. 8·5 c.c. of decinormal sulphuric acid were neutralised by the ammonia evolved during two hours and a half. Hence 0·0144 gram of ammonia had been produced, which corresponds with a formation of 0·0059 gram of NH_3 per hour.

I hope to complete this research by investigating the influence of temperature, proportion of N to H, quantity of spongy metal present, rapidity of current of gas passing through the apparatus, and especially the action of *spongy palladium* and other substances, with a view to ascertain the most favourable conditions for the *maximum production of ammonia by synthesis.*

XXIII.—*On the Synthesis of Ammonia.*

By George Stillingfleet Johnson, King's College, London.

(Second Notice.)

My demonstration of the synthetical production of ammonia from the nitrogen evolved by heating a solution of nitrite of ammonium by passing it mingled with hydrogen over spongy platinum, after removing adhering ammonia from it by sulphuric acid (demonstrated to this Society January 20th, 1881), having been objected to on the ground that the vapour of some ammoniacal salt might be carried by the rapid stream of gas through the absorbing apparatus and the first Nessler solution, and might then be dissociated in the hot platinum-tube and yield ammonia which would tinge the Nessler solution be-

yond, I made the following experiment with a view to elucidate this matter:—

I passed hydrogen through the apparatus described in my last paper and over the spongy platinum, heating the latter till it gave off no ammonia, as shown by the absence of precipitation in a Nessler solution through which the gas was made to pass; I then allowed the platinum to cool in the hydrogen, and introduced a current of *nitrogen* from a mixture of nitrite of potash and sal-ammoniac, with the intention of displacing all the hydrogen from the apparatus whilst the platinum remained *cold*, and then heating the platinum, so that the ammonia salt (if present) might be dissociated and yield the ammonia, which would then show itself in the second Nessler bulb, though no hydrogen was passing through the apparatus. I was surprised, however, to find that a copious precipitate appeared in the Nessler bulb immediately after the admission of the nitrogen into the apparatus, though the platinum remained cold; and on adjusting a set of bulbs containing decinormal sulphuric acid and passing the mixed gases for one hour, I found that acid had been neutralised corresponding with a production of 24 mgrms. of ammonia. The dissociation of vapour of an ammoniacal salt in *cold* spongy platinum does not seem probable.

It was desired that I should make some experiments with nitrogen obtained from a non-ammoniacal source, and accordingly I attempted to synthesise ammonia with nitrogen procured from atmospheric air by the action of heated copper. In this I was not successful.

I next passed the nitrogen from ammonium nitrite over heated copper, and subsequently through spongy platinum with hydrogen, and obtained no ammonia whatever.

This result might be due either to the nitrogen being rendered inactive by heat, or to the removal by the red-hot copper of some *oxide of nitrogen* which had previously yielded the ammonia.

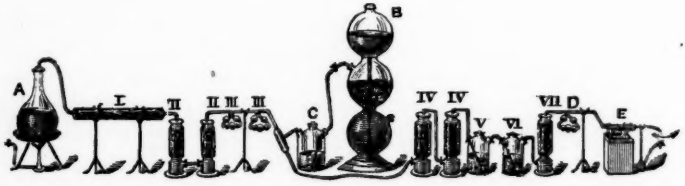
Now it has long been known that the nitrogen obtained by heating a solution of ammonium nitrite is liable to be contaminated with nitric oxide whenever, as frequently happens, the evolution of gas becomes unusually violent, red fumes being constantly observed upon contact of the rapidly evolved gas then produced with atmospheric air.

But I have found that in all cases, and however carefully regulated the temperature and rapidity of evolution of gas may be, the nitrogen from this source is invariably accompanied by small quantities of nitric oxide, and the complete removal of this impurity is a matter of no little difficulty.

I employed a solution of *ferrous sulphate* for this purpose, and passed the nitrogen through a counterpoised tube containing freshly reduced copper, the copper being heated to redness, allowed to cool in the nitrogen, and weighed at intervals of one hour.

The increase in weight of the copper was reduced to 5 mgrms. per hour, when the absorbing apparatus consisted of three French drying-tubes containing pumice soaked with acid ferrous sulphate, two potash-bulbs containing acid solution of ferrous sulphate, and one Woulffe's bottle containing the same absorbent.

The copper increased in weight *not at all* when heated for one hour in a constant current of the gas from a solution of nitrite of potash and ammoniac, which has been passed through (1) a long tube, (2) two French drying-tubes, all packed with fragments of pumice-stone soaked in a saturated acid solution of ferrous sulphate; (3) two potash-bulbs containing acid solution of ferrous sulphate; (4) two more French drying-tubes prepared in the same way as the first; (5) a Woulffe's bottle containing acid ferrous sulphate; (6) a Woulffe's bottle containing potash and pyrogallin; and (7) a French drying-tube containing pumice soaked in oil of vitrol.



A. Solution of Nitrate of Potash and Sal-ammoniac. B. Hydrogen Apparatus. C. Solution of Nitrate of Silver. D. Nessler test. E. Spongy Platinum.

Having, by means of this elaborate absorbing apparatus, removed all traces of oxides of nitrogen, and obtained a gas which gave up nothing to red-hot copper (evidently perfectly pure nitrogen), I now admitted hydrogen into the apparatus through a solution of nitrate of silver, and the same absorbing apparatus as the nitrogen from (4) onwards; and, on passing the mixed gases over spongy platinum, I obtained ammonia as before.

I first passed the mixed gases over the *cold* spongy platinum for one hour, and absorbed the ammonia by normal sulphuric acid. Acid was neutralised corresponding with a production of 3 mgrms. of ammonia.

In a subsequent experiment in which the platinum was heated to dull redness, and the gas was passing at the same pace, an exactly equal weight of ammonia was produced in one hour.

It was impossible in these experiments to pass the gas very rapidly through the apparatus, owing to the great pressure to be overcome by the various liquids it had to traverse. Hence the comparatively small formation of ammonia. I next passed the nitrogen through the same absorbing apparatus, and mixed with hydrogen over heated asbestos, then over cold spongy platinum, and finally through a Nessler solution.

Traces of ammonia were produced in the hot asbestos,* but these were retained by a tube containing pumice and sulphuric acid placed between the asbestos and spongy platinum tubes. It was found that *no* ammonia was produced as long as the asbestos-tube remained hot, but the Nessler solution began to become turbid as soon as this tube could be touched by the fingers, and then soon showed evidence of the formation of ammonia.

In order to ascertain whether the absorbing apparatus still retained its efficiency, the nitrogen was now allowed to displace all hydrogen from the front of the apparatus, and the copper tube was again heated for half an hour to redness, and allowed to cool in the gas. Its *weight was unchanged.*

Having thus obtained ammonia by synthesis from hydrogen, and a gas evolved from a solution of nitrite of potash and sal-ammoniac, and which yielded nothing to red-hot copper (presumably pure nitrogen), and having found that the formation of ammonia is arrested by passing this gas through a red-hot tube, the evidence seems very strong that nitrogen, like phosphorus, is capable of existing in two forms, an active one and an inactive one, the latter produced by heat.

I hope to pursue this subject by investigating the behaviour of nitrogen from other sources, and especially of atmospheric nitrogen obtained without the aid of heat, when brought in contact with spongy platinum in presence of hydrogen.

XXIV.—*Researches on the Laws of Substitution in the Naphthalene Series.* No. I.

By Henry E. Armstrong, F.R.S.

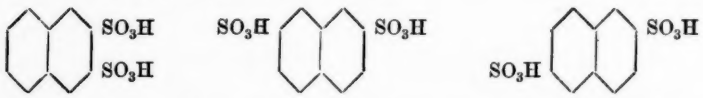
The product of the action of sulphuric acid in excess on naphthalene at a somewhat elevated temperature consists, according to Ebert and Merz (*Ber.*, **10**, 592), of *two* isomeric disulphonic acids, which furnish lead metallic salts, chloride, and amide, differing considerably in crystalline form, solubility, amount of water of crystallisation, &c. They are also sharply distinguished by their behaviour on fusion with potassium hydroxide, the one—the so-called α-disulphonic acid—yielding a corresponding dihydroxynaphthalene, $C_{10}H_6(OH)_2$; the other, betanaph-

* Ammonia was also formed in many experiments, when mixed nitrogen and hydrogen were passed over heated freshly reduced *copper*. The production always ceased when the nitrogen was passed *alone* through the apparatus, till all hydrogen had been expelled.

tholsulphonic acid, $C_{10}H_6(OH)(SO_3H)$. This latter acid was regarded by Ebert and Merz as identical with that produced on treating betanaphthol with sulphuric acid.

In the latter part of the year 1879, when preparing an article on Naphthalene for the forthcoming new supplement to *Watts's Dictionary of Chemistry*, I had occasion to discuss the constitution of the naphthalene derivatives, including these disulphonic acids. The following passage from the article in question may be here cited, as the conclusions then arrived at led to the experiments to be described in this communication :—

"δ- and ϵ-dichloronaphthalene, which are derived from the isomeric naphthalenedisulphonic acids, are probably, one or both, $\beta\beta$-derivatives. Both the disulphonic acids are probably derived from the β-monosulphonic acid (being formed at an elevated temperature); but supposing this to be the case, and that the β-disulphonic acid contains both sulpho-groups in β-positions, there are still three formulæ which may be applied to it, viz.:



"According to Ebert and Merz, the naphtholsulphonic acid formed on fusing the β-disulphonate with potassium hydroxide is identical with that produced from betanaphthol and sulphuric acid; if this be the case, the first of the above formulæ would appear to be the most probable, for as the action of sulphuric acid and bromine on the phenols is similar, in so far as the constitution of the resulting compounds is concerned, as betanaphthol yields a bromo-derivative in which both bromine and the OH-group are in the same C_6-group (Smith, *Chem. Soc. Trans.*, 1879, 789), it is probable that the sulphonic acid derived from betanaphthol would contain both the OH- and the sulpho-group in the same C_6-group. If, however, the β-disulphonic acid were thus constituted, the dicarboxylic acid derived from it should be identical with naphthophthalic acid, $C_{10}H_6(COOH)_2$, which is not the case. It is therefore a question whether the naphtholsulphonic acid from the β-disulphonic acid and that from betanaphthol are identical, as Ebert and Merz have stated, or whether isomeric change does not take place in some of the reactions above referred to. The fact that it is the C_6-group which does not contain the sulpho-group that is attacked when naphthalene-α- and β-sulphonic chlorides are submitted to the action of chlorine, or when naphthalene-α-sulphonic acid is treated with nitric acid, renders it probable that the naphthalenedisulphonic acids also contain the sulpho-groups in distinct hexagons (this expression, of course, merely has reference to the

symbols), and such a conclusion would appear to harmonise well with their general behaviour and that of the compounds derived from them. On this assumption the second and third of the formulæ given above are the most probable expressions of the constitution of the α- and β-disulphonic acids respectively."

As a first step towards the solution of the problem here indicated, it appeared desirable to verify the conclusion arrived at by Ebert and Merz, who do not appear to have themselves compared the betanaphtholsulphonic acid they obtained with that previously prepared by Schaeffer (*Annalen*, **152**, 296) from betanaphthol, but to have concluded that the two products were identical on the grounds that their acid crystallised in plates melting at 122°, that obtained by Schaeffer being described as crystallising in plates melting at 125°; and that it exhibited the same reactions with ferric chloride and with nitric acid as Schaeffer's product. The only salt they describe is the potassium salt, which was not prepared by Schaeffer.

In conjunction with Mr. N. C. Graham, I therefore commenced experiments having this end in view. Subsequently we directed our attention to the investigation of the betanaphtholsulphonic acids, as it was to be expected that results of interest would accrue from the examination of derivatives of a phenol which in some respects behaves as no other known phenol, the determination of the constitution of the β-naphthaquinone of Stenhouse and Groves being a problem of peculiar interest. Lastly, the dihydroxynaphthalene described by Ebert and Merz claimed our attention. The results we have obtained are in part so remarkable, and necessitate so large an extension of the investigation as originally planned, that it appears to me desirable to publish them as a preliminary communication.

Betanaphthol-α-sulphonic Acid from Betanaphthol and from Naphthalenedisulphonic Acid.

By Henry E. Armstrong, and N. C. Graham.

We have found that instead of neutralising the crude product of the action of sulphuric acid on betanaphthol at 100° with lead carbonate, &c., as recommended by Schaeffer, it is preferable to employ calcium carbonate. The calcium betanaphthol-α-sulphonate readily crystallises from the properly concentrated solution, and may without difficulty be purified by recrystallisation and the aid of animal charcoal. A much smaller proportion of sulphuric acid than is recommended by Schaeffer may with advantage be employed, but we reserve further particulars for a future communication.

Calcium Betanaphthol-α-sulphonate, $[C_{10}H_6(OH)(SO_3)]_2Ca + 5OH_2$. This salt ordinarily crystallises in the manner described by Schaeffer;

it may also be obtained in massive, but most irregularly formed prismatic crystals by allowing the cold saturated solution to evaporate spontaneously. Although it becomes slightly brown on heating at 100°, no sensible amount of decomposition takes place at this temperature, and the water of crystallisation may safely be determined in the usual manner. The results of our analyses agree with Schaeffer's formula given above.

Potassium Betanaphthol-α-sulphonate, $C_{10}H_6(OH)(SO_3K)$.—This salt is readily prepared from the calcium salt and potassium carbonate. It crystallises with varying amounts of water and in various forms, according to the conditions. By allowing not too small a quantity of a hot saturated solution to cool slowly, it may usually be obtained in groups of transparent, well-defined, elongated prisms, pointed at the end, and apparently square in section; these crystals contain about 3 per cent. of water, but on exposure to the air they gradually become opaque from loss of water. More frequently it separates in less well-defined, more plate-like prismatic forms, which appear always to contain less water—a little over 1 per cent.—and these remain unaltered on exposure to air. Potassium betanaphthol-α-sulphonate is less soluble than the calcium salt, dissolving only to the extent of about 2 parts in 100 of water at 15°. An aqueous solution exhibits a faint blue fluorescence, which is much intensified by the addition of ammonia. As commercial betanaphthol was employed in the preparation of the acid, we were at first inclined to regard this fluorescence as accidental, but as the salt which has been several times crystallised also exhibits it, and as all other salts we have prepared of the acid are also fluorescent, there can be little doubt that it is a specific character of the betanaphthol-α-sulphonates. According to Griess (*Ber.*, **13**, 1959), the betanaphtholdisulphonates are also fluorescent, especially in presence of ammonia.

Barium Betanaphthol-α-sulphonate, $[C_{10}H_6(OH)(SO_3)]_2Ba + 6OH_2$. —This is by far the most characteristic of the betanaphthol-α-sulphonates. It is readily prepared by precipitating a hot saturated solution of the calcium salt with barium chloride. If the boiling saturated solution be allowed to cool very slowly, it separates in transparent well-developed long narrow prisms. Like the calcium salt, it parts with its water of crystallisation when introduced into hot water, and the anhydrous salt then dissolves with extreme difficulty.

Betanaphtholsulphonic Acid from Naphthalene-β-disulphonic Acid.—Following Ebert and Merz's directions, naphthalene was heated with five times its weight of sulphuric acid at 180° during about 24 hours. The least soluble portion of the mixture of calcium salts obtained on neutralising with calcium carbonate was converted into potassium salt, and the latter fused with 2—3 times its weight of potassium

hydroxide. The naphtholsulphonate obtained did not, however, agree in appearance with that from betanaphthol, and always crystallised in less well-defined forms; but its solubility in cold water was the same, and all doubt as to the identity of the two products was removed on treating it with bromine. The salt obtained had the same composition as the bromobetanaphtholsulphonate prepared from betanaphthol described later on. It crystallised in the same unmistakeable forms; it had the same solubility; and, lastly, the calcium salt produced by precipitating its solution with calcium chloride crystallised from water in the thin micaceous plates characteristic of calcium bromobetanaphthol-α-sulphonate.

On the Action of Bromine, Chlorine and Nitric Acid on Potassium Betanaphthol-α-sulphonate. By the Same.

Potassium Bromobetanaphthol-α-sulphonate, $C_{10}H_5Br(OH)(SO_3K) + 2OH_2$.—This salt is readily prepared by adding the calculated amount of bromine to a cold saturated solution of potassium betanaphthol-α-sulphonate. The bromine is rapidly absorbed on agitating the liquid, and the greater part of the bromo-salt at once separates in glistening scales; it is readily purified by recrystallisation from boiling water. It crystallises from a hot saturated solution in broad, transparent, well developed prisms and plates of considerable thickness; usually a number of isolated rhombus-shaped plates form on the side of the beaker. Although very sparingly soluble in cold water, 100 parts of which at 15° dissolve only about 0·4 part anhydrous salt, it is moderately soluble in water at 100°. It does not manifest any tendency to effloresce on exposure to air. When heated with dilute nitric acid, it yields a yellow solution. By boiling with nitric acid and subsequent evaporation on the water-bath, it is oxidised to phthalic acid.

Calcium Bromobetanaphthol-α-sulphonate, $[C_{10}H_5Br(OH)(SO_3)]_2Ca + xOH_2$.—This salt was prepared in the same way as the potassium salt. It is very slightly soluble in cold water, and not much more so in boiling water; nevertheless it separates with remarkable slowness from a hot saturated solution, crystallising in aggregates of extremely thin micaceous plates. These aggregates mostly exhibit a characteristic serrated outline, and a broad spear-shaped termination. On removal from the liquid the crystals rapidly become opaque from loss of water of crystallisation.

If potassium betanaphthol-α-sulphonate be submitted to the action of bromine in the proportion of 1 mol. of the former to 2 mols. of the latter, a dibromosulpho-salt is produced, but it is somewhat difficult when operating in aqueous solution to avoid the formation of coloured products. This salt is more soluble than the monobromo-salt, and

crystallises in a less characteristic manner, but it may be obtained perfectly colourless.

We have not succeeded in preparing a tribromosulpho-salt by the action of bromine in the proportion of 3 mols. to 1 mol. of beta-naphthol-α-sulphonate. The product is apparently a mixture of the products of the action of 2 mols. and of 4 mols. of bromine.

If an acetic acid solution of potassium betanaphtholsulphonate be treated with bromine in the proportion of 1 mol. to 4 mols., a deep yellow-coloured solution is obtained which remains clear on the addition of water; if the acid be evaporated off on the water-bath and the residue be boiled with water, it dissolves with the exception of a relatively small amount of a yellow substance soluble in acetic acid, and as the solution cools a potassium sulpho-salt crystallises out in glistening dark-yellow plates not unlike chloranil in appearance, but of darker colour. This substance forms a deep blood-red coloured solution; it is readily soluble in boiling water, but only moderately in cold water. Bromine and potassium determinations coincide with the formula $C_{10}H_4BrSO_6K$; the air-dry salt contains in addition the elements of a molecule of water. The only probable formulæ for a body of this composition produced in such a manner are the following:

$$C_{10}H_4(O_2)(OBr).SO_3K \text{ and } C_{10}H_3Br(O_2)(OH).SO_3K.$$

The first is that of a *potassium bromoxylnaphthaquinonesulphonate*, and is, we think, to be preferred, as there is no evidence of the production of a tribromobetanaphthol-α-sulphonate, as should be the case if the second formula were a correct expression of the constitution of our salt.

Bromine has no further action on this salt at 100° in presence of water.

A corresponding chloro-compound is obtained on saturating an acetic acid solution of potassium betanaphthol-α-sulphonate with chlorine. It very closely resembles the bromo-compound in appearance and properties. The action of iodine does not appear to extend so far as that of chlorine or bromine.

No effect is produced on adding nitric acid to a cold solution of a betanaphthol-α-sulphonate, but on the application of heat the liquid assumes a magnificent carmine-red colour, as already noticed by Schaeffer. A small amount of a red crystalline substance is gradually deposited from the solution, and a further small amount is precipitated on the addition of common salt solution; it has little tinctorial power and is very unstable. The chief product remains in solution. If a solution of potassium betanaphthol-α-sulphonate be mixed with nitric acid in the proportion of 1 mol. to 4 mols. and evaporated to dryness on the water-bath, vigorous action ensues, and a dark-coloured residue

finally remains which is almost entirely soluble in water but very difficult to crystallise. Its solution has an intense red colour similar to, but much deeper in shade than, that of the bromo-salt above described, and it is highly probable that it is an allied substance; that, in fact, it is a hydroxynaphthaquinonesulphonate of the formula $C_{10}H_4(O_2)(OH).SO_3K$. We hope either to obtain this body from hydroxy-α-naphthaquinone (naphthalic acid), or to succeed in converting it into this latter compound.

We have also prepared the barium betanaphtholdisulphonates recently described by Griess (*Ber.*, **13**, 1956), and submitted them to the action of bromine. In the first instance, they yield monobromo-derivatives, but, apparently, they ultimately furnish the same product as a betanaphthol-α-sulphonate. It is noteworthy that neither of the disulphonates exhibits a characteristic reaction with nitric acid, their solutions being merely coloured yellow when warmed with the acid.

On Dihydroxynaphthalene from Naphthalene-α-disulphonic Acid.
By the Same.

Ebert and Merz are so specific in their statement that naphthalene yields two disulphonic acids, and that only one of these is convertible into a corresponding dihydroxynaphthalene, that we did not consider it necessary to prepare pure naphthalene-α-disulphonate, but fused the potassium salt from the more soluble portion of the mixture of calcium salts obtained by neutralising the crude mixture of acids formed on heating 1 pt. of naphthalene with 5 pts. of sulphuric acid at 160° for about four hours. The product, although moderately soluble in boiling water, was very slightly soluble in cold water; it crystallised in fine white needles.

On warming it with twice its weight of sulphuric acid on the water-bath for a few minutes, it was completely converted into sulphonic acid, the mixture, which was liquid at first, solidifying to a but slightly coloured mass of crystals almost entirely soluble in water. The solution was neutralised with calcium carbonate and evaporated to a small bulk; on cooling, it solidified to a mycelium-like mass of extremely fine long prismatic crystals very easily soluble in water. The barium salt, prepared in a similar manner, is also very soluble, but crystallises on slow evaporation of the solution in well-defined prisms. Both salts contain water of crystallisation; the anhydrous salts gave numbers on analysis indicating that they are *tetrasulphonates*. On treatment with an excess of bromine, a solution of the calcium salt furnishes a precipitate consisting of fine white needles precisely similar to tribromophenol. The product is free from sulphur, and is evidently a highly brominated derivative of the parent phenol, as it contains over 70 per

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cent. of bromine. By the employment of less bromine, bromosulpho-salts are obtained which, on treatment with nitric acid, yield several bromonitro-derivatives closely resembling those obtained in a similar manner from the bromophenolsulphonates. Nitric acid also converts the original sulpho-salt into nitrosulpho-salt, or a nitro-derivative of the parent phenol, according to the proportion employed. In short, the dihydroxynaphthalene in question exhibits precisely the behaviour of phenol itself. The amount of material at our disposal has been too small to admit of the complete elucidation of the nature of the reactions here indicated, but we trust soon to be in a position to continue their examination.

Dr. Griess has recently described (*Ber.*, **13**, 1959) a dihydroxynaphthalenedisulphonic acid, prepared from a commercial product obtained from Dr. Caro. As, according to Ebert and Merz, only one of the two disulphonic acids from naphthalene yields a dihydroxynaphthalene on fusion with potassium hydroxide, we at first supposed that we were operating with the same substance, but it soon became obvious that this could not be the case, and on sending a specimen of our product to Dr. Griess, he at once informed us that it was quite different from the dihydroxynaphthalene he had used. We were thus led to contrast Ebert and Merz's statements with those of previous workers in the same field more carefully than we had previously done, and soon came to the conclusion that the observations of Dusart (*Compt. rend.*, **64**, 859), and of Darmstädter and Wichelhaus (*Annalen*, **152**, 306), could not be reconciled with those of Ebert and Merz. Two explanations were possible, (1) that by the action of sulphuric acid on naphthalene, not two, but three, isomeric disulphonic acids are produced, two of which are convertible into corresponding dihydroxynaphthalenes, the third yielding betanaphthol-α-sulphonate on fusion with potassium hydroxide; (2) that only two disulphonic acids are produced, and that both may be converted into corresponding dihydroxynaphthalenes, *i.e.*, the sulpho-group in the betanaphthol-α-sulphonates *may* be displaced by OH. We believe that we are justified in regarding the first and the latter part of the second of these propositions as true.

By submitting the potassium salt prepared from the portion of medium solubility of the crude mixture of calcium naphthalenedisulphonates to the action of fused potassium hydroxide, we have succeeded in obtaining a product in all respects identical with that employed by Griess, and entirely different from the dihydroxynaphthalene which we had previously prepared, but agreeing fairly well in properties with the descriptions given by Dusart, and Darmstädter and Wichelhaus, of their products.

Secondly, we find that it *is* possible to decompose potassium beta-

naphthol-α-sulphonate by fused potassium hydroxide, although great care is necessary in conducting the operation. If the melt be dissolved in water, and the solution mixed with an excess of hydrogen chloride, much sulphur dioxide is evolved, and a small quantity of resinous matter separates out; if the hot liquid be rapidly filtered and then left to cool, a considerable quantity of a grey precipitate is deposited. On digesting this precipitate with warm ether, filtering, and evaporating the solution, a brown crystalline residue is obtained, which dissolves with considerable difficulty in hot water; the solution is decolorised by digestion with animal charcoal, filtered boiling hot, and then allowed to cool slowly. Two substances ultimately crystallise out: the one in the form of minute glistening scales, the other in the form of brownish, transparent, prismatic crystals, which often present a peculiar dagger-shaped outline. They may be almost entirely separated by levigation. We have not yet determined the composition of either of these substances, the quantity at our disposal being too small.

The dihydroxynaphthalene first prepared by us crystallises from water in long fine needles, melting at 158°; its alkaline solution remains colourless, even after long exposure to the air. That employed by Griess is more soluble, especially in cold water, and crystallises in thin glistening plates of considerable size; when heated in a fine tube, it blackens without melting, at a temperature below 200°, but melts when heated quickly on platinum foil; its alkaline solution remains colourless on exposure to the air, but acquires a magnificent red colour on the addition of a minute quantity of orthodiazophenolsulphonate, this last reaction being remarkably characteristic,* and not exhibited by the isomeride, which is unaffected by the diazo-body in question; lastly, on the addition of bromine-water to its aqueous solution, a brilliant yellow precipitate is thrown down, which, however, gradually darkens in colour.

The two products from potassium betanaphthol-α-sulphonate possess somewhat different properties. That crystallising in small scales appears to be much less soluble in water than the substance employed by Griess; it dissolves in alkali, forming a brown solution, which darkens on exposure to the air. That crystallising in prisms is characterised by a magnificent blue fluorescence produced on adding alkali to its aqueous solution; at the same time, the liquid becomes brown. By this reaction we have ascertained that the substance resembling that employed by Griess, which we prepared, was distinctly contaminated with this particular product of the action of potassium hydroxide on potassium betanaphtholsulphonate. The alkaline solutions of both products from the betanaphthol-α-sulphonate are coloured red on the addition of orthodiazophenolsulphonate, but the colour is fugitive.

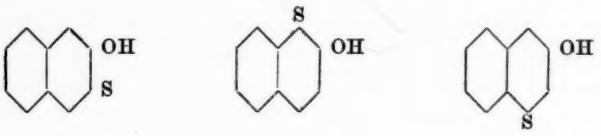
* We are indebted to Dr. Griess for acquainting us with this reaction.

Cleve has stated (*Bull. Soc. Chim.*, **25**, 244), that naphthalene-β-disulphonic acid yields a dichloronaphthalene, melting at 135°, when distilled with phosphorus pentachloride. In order further to confirm the relation between naphthalene-β-disulphonic acid and betanaphthol-α-sulphonic acid, we treated a small quantity of the potassium salt of the latter acid in like manner, and obtained a product possessing the properties assigned by Cleve to the dichloronaphthalene in question.

Theoretical Considerations. By HENRY E. ARMSTRONG.

The facts brought to light by the experiments above described are not without interest with reference to the problems indicated in the commencement of this communication.

Betanaphtholsulphonic acid and the naphthalenedisulphonic acid from which it may be formed by displacement of one of the SO_3H groups by OH obviously are similar in constitution, unless indeed isomeric change take place in the conversion of the one into the other, which is improbable. As I have already stated, our prior knowledge appears to warrant the conclusion that the OH and SO_3H groups are both contained in the one C_6-group, and this is shown to be the case by the formation of phthalic acid from bromobetanaphthol-α-sulphonate, and from nitrosobetanaphthol-α-sulphonate (Meldola, this Journal, **39**, 46). Regarding the relative position of the OH and SO_3H groups, the last of the three formulæ (S = SO_3H):



may be pronounced quite out of question, as the group SO_3H in all cases tends to occupy either the ortho- or the para-position relatively to an OH-group; and No. 1 I am inclined to regard as the far more probable of the two remaining formulæ, as there appears to be a special tendency in the naphthalene series for bodies having symmetrical formulæ to be produced. The formation of a compound which there can be little doubt is an α-naphthaquinone derivative by the action of bromine on potassium betanaphtholsulphonate, lends considerable support to this view. If the conclusion thus arrived at be correct, naphthalene-β-disulphonic acid is represented by formula I, p. 134.

The constitution of the dihydroxynaphthalene of Ebert and Merz, and of the corresponding naphthalenedisulphonic acid, has yet to be finally determined, but judging from its general behaviour, it can hardly be doubted that the former is an $\alpha\alpha$-derivative of naphthalene,

and that the disulphonic acid in question has the constitution represented by one or other of the following formulæ:

The dihydroxynaphthalene of Dusart and of Darmstädter and Wichelhaus (that employed by Griess) probably has one or both of its OH-groups in the β-position, as it readily furnishes coloured derivatives with diazo-compounds, in which respect it resembles betanaphthol.

Assuming the two bodies obtained on fusing potassium betanaphthol-α-sulphonate with potassium hydroxide to be dihydroxynaphthalenes, one—perhaps that characterised by the blue fluorescence—is probably formed by the direct displacement of the SO_3H-group by OH. On this view, it appeared not unlikely that it was identical with β-naphthaquinol, but on dissolving a small quantity of β-naphthaquinone in sulphurous acid, and then adding alkali, not the slightest fluorescence was visible. It is possible, however, that the action of nitrous acid on betanaphthol does not strictly correspond with that of bromine and sulphuric acid, and that the nitrosobetanaphthol, from which β-naphthaquinone is formed is an $\alpha\beta$-derivative. The formation of a second dihydroxynaphthalene from betanaphthol-α-sulphonate would involve a reaction more than once observed in the anthracene series, viz., the direct introduction of an OH-group in place of an atom of hydrogen, and the displacement of the SO_3H-group by hydrogen. It is noteworthy that hydrogen is slowly evolved, almost from the beginning of the fusion process.

XXV.—*The Action of Hydrochloric Acid on Ethylene Alcohol.*

By C. Schorlemmer, F.R.S.

On saturating this glycol, $C_2H_4(OH)_2$, with the gaseous acid, and heating the mixture to 100°, it is, as Wurtz has shown, converted into ethylene chlorhydrate, $C_2H_4Cl(OH)$, whilst by the action of phosphorus pentachloride the alcohol is transformed into ethylene dichloride (*Ann. Chim. Phys.* [3], **55**, 418).

From these facts the conclusion has been drawn that, by means of

hydrochloric acid, only one hydroxyl could be replaced by chlorine, and consequently that its functions were different from those of the second. As this view is still maintained in modern handbooks (Kolbe, *Org. Chem.*, 2nd Ed., by v. Meyer, **1**, 275), and as I could not agree with it, I set to work in order to settle this point.

The reason why, in the experiment of Wurtz, the reaction did not extend to the second hydroxyl is obvious; he did not use an excess of the acid, and had to repeat the above treatment several times before all the glycol was converted into the chlorhydrate. It seemed more than probable that by employing a larger proportion of the acid, ethylene dichloride would be formed. I therefore enclosed some glycol with an excess of fuming hydrochloric acid in a sealed tube, and heated in a steam-bath. After some time the clear liquid became turbid, and a heavy oily liquid separated out, the quantity increasing until its bulk was about equal to that of the glycol employed.

This oil being washed with water, and dried over potassium carbonate, boiled at 83—85°, and exhibited all the characteristic properties of ethylene dichloride.

XXVI.—*On the Estimation of Organic Carbon and Nitrogen in Water Analysis, simultaneously with the Estimation of Nitric Acid.*

By M. Whitley Williams.

A great deal of attention has lately been given to the estimation of the organic matter existing in natural waters, and many processes have recently been devised by which either the carbon or the nitrogen of the organic matter, or both, may be determined with a greater or less degree of accuracy. Of all the processes in use perhaps the safest and most thoroughly scientific in principle is that originally described by Frankland and Armstrong, in 1868 (*Chem. Soc. J.*, 1868, 77). A complete account of this process, together with the most recent modifications and improvements, is to be found in the *Handbook of Water Analysis*, lately published by Frankland (London, 1880). Briefly described, it consists in first evaporating the water to dryness, with the addition of sulphurous acid to decompose and dissipate the nitric acid, and expel carbonic acid, and then burning the dry residue with oxide of copper and metallic copper *in vacuo*. The carbon and nitrogen of the organic matter are calculated from the volumes of carbonic

acid and nitrogen contained in the gases resulting from the combustion.*

The evaporation with sulphurous acid is undoubtedly the least satisfactory part of this process, and many objections more or less valid have been urged against it by numerous authors. A litre of water requires over 24 hours' continuous evaporation, and when the amount of nitrates is at all large, repeated evaporations with fresh quantities of sulphurous acid are necessary to complete their decomposition, so that the process becomes protracted to a tedious length. Prolonged heating with sulphurous acid may itself decompose organic bodies, but the process is more objectionable because a portion of the sulphurous is transformed into sulphuric acid by the oxygen of the air, and unless care be taken that a sufficient quantity of bases are present to neutralise this strong acid, the organic matter in the residue would be charred by it. There is, moreover, no test by which to make certain that the nitric acid has been completely destroyed or expelled, and since its destruction is only slowly effected by sulphurous acid, there is no security that the residue will be free from all traces of it. But sulphurous acid has still greater faults. When the water contains any appreciable amount of ammonia, a portion only of this ammonia is found in combination with sulphurous acid in the water residue, while another and variable portion is lost by dissociation of the ammonic sulphite during evaporation. A correction of considerable magnitude has therefore to be calculated, according to an empirical method, and applied to the organic nitrogen (Frankland's *Water Analysis*, pp. 81 and 108), and this correction necessarily involves an increased error in the result of the analysis. There is another possibility of serious error which has hitherto been overlooked. Sulphurous acid destroys nitric acid by reducing it to lower oxidised nitrous compounds, which escape in the gaseous state. Now, it is well known that nitrous acid attacks ammonia and amidated bodies in acid solutions, evolving their nitrogen in the free state; and it is uncertain how far the nitrogen of the ammonia and of the organic matter in a water undergoing evaporation may be attacked in this way by the products of the action of sulphurous acid upon the nitrates.

Prof. Frankland himself appears desirous of avoiding the use of sulphurous acid as far as possible, and he has recommended the employment of borax and phosphoric acid in a few cases in which sulphurous acid can be dispensed with.

There is, however, a simple method of entirely avoiding the use of sulphurous acid, which I shall proceed to describe.

If it were possible to convert the nitric acid in a water completely into ammonia, without adding any substance likely to interfere with

* This process of course pretends to estimate only the non-volatile organic matter.

the evaporation to dryness, or with the subsequent combustion of the water-residue, it would be easy to remove the ammonia formed from the nitrates, together with that pre-existing in the water, by simple distillation. The water could then be evaporated to dryness, and the residue obtained in a state fit for combustion, free from all ammoniacal and nitrous compounds. Thus sulphurous acid would not be required to destroy the nitric acid, nor would the results of the analysis require any correction, either for the ammonia pre-existing in the water, or for that lost by dissociation during evaporation.

The copper-zinc couple is an agent by which such a transformation of nitric acid can be effected. It acts by decomposing water, with formation of oxide of zinc and liberation of hydrogen, and the nitric acid is converted into ammonia by this hydrogen; it therefore adds nothing to the solution, and nothing is abstracted by it, save, perhaps, that the oxide of zinc may absorb a certain amount of any carbonic acid present. In my former paper I have shown that even the most dilute solutions of a nitrate can be completely reduced by the couple in a reasonable time; and it therefore seemed probable that the copper-zinc couple could be used for eliminating the nitrates in a water prior to the estimation of the organic carbon and nitrogen. Upon trial I found that it could be applied to this purpose with great advantage, not only because the process was shortened, but because the estimation of the nitric acid could be combined with that of the organic elements in the one operation.

The process is conducted in the following manner. The zinc foil to be employed must first be carefully cleansed from grease and other organic matters by boiling with dilute caustic alkali, and after the alkali has been washed away, its surface should be freed from oxide by washing with acidulated water. It may then be placed in a wide-mouthed stoppered bottle, and made into "couple" in the manner and with the precautions mentioned in my former paper (this Journal, p. 109). The couple having been made and washed with distilled water, is next washed with a quantity of the water to be analysed, in order to displace the adhering distilled water; this washing is thrown away, and the requisite amount of the water is then poured on and allowed to digest at a proper temperature, until the reduction of the nitric acid is complete. The bottle should be quite filled with the water. In the previous paper several methods have been pointed out by which the transformation into ammonia may be hastened, among which the most important are the addition of a little sodium chloride or of carbonic acid, and the raising of the temperature. When a litre of the water is to be evaporated for the estimation of the organic matter, about 1,200 or 1,300 c.c. should be subjected to the action of the couple, and the amount of zinc-foil used with it should be regulated

by the richness of the water in nitrates, and by the directions given in my former paper (p. 109).

After the water has digested over night or for a reasonable time, it should be tested to ascertain whether the nitric acid has been wholly transformed into ammonia. The experiments given in my former paper show that nitrous acid does not entirely disappear from the solution until all the nitric acid has been transformed. By taking advantage of this fact, and using Peter Griess's very delicate test for nitrous acid, the end of the reaction may be ascertained with great precision. 100 c.c. of the water should be withdrawn and metaphenylene diamine and sulphuric acid added to it. If any trace of a yellow coloration be found after half an hour's standing, the water should be allowed to digest upon the couple for a longer time. Should there be no coloration, the reaction is completed, and the estimation of the nitric acid can, if desired, be made at this stage by directly titrating the ammonia in a measured portion of the water with Nessler's reagent. If any difficulty be found in the direct titration, the ammonia may be estimated in the distillate obtained in the subsequent part of the process.

The reaction being concluded, the remainder of the water is poured off the couple into a clean tall cylinder, and allowed to stand for a few minutes,.so that any floating particles of copper or oxide of zinc may subside. Sometimes the water is hazy with very finely divided oxide of zinc, but this can be neglected, since it in no way interferes with the subsequent steps of the process. A litre of the water, or as much as may be required, is decanted from the cylinder, poured into a clean glass retort, and distilled until the distillate is quite free from ammonia. I have usually added one or two drops of a concentrated solution of sodium carbonate, or a fragment of pure lime, in order to insure that all the ammonia shall be free to volatilise. The ammoniacal distillate obtained in this part of the process may be used with advantage for the estimation of the nitric acid. The first distillates are somewhat concentrated, and to prevent any loss of ammonia, the beak of the condenser should dip into a little dilute hydrochloric acid.

The ammonia having all been distilled off, the water in the retort is further distilled to as low a bulk as may be desired. It may usually be concentrated to 200 c.c. or even 100 c.c. with perfect safety. During the distillation, a certain amount of carbonate of lime will in many cases be deposited upon the sides of the retort. To dissolve this and to expel the carbonic acid from the residue, the addition of some acid is necessary. Phosphoric acid may be used for this purpose, but there is little or no objection to the use of a little sulphurous acid at this stage of the process. If the latter acid be employed, it is only necessary to add sufficient to dissolve the carbonate of lime, and boil the

solution briskly for a few minutes, to effectually expel the carbonic acid. The solution is then poured into a smooth hemispherical basin, the retort rinsed out with a little pure distilled water, and the whole evaporated to dryness on the water-bath. The residue thus obtained is free from all compounds of nitrogen, except the organic matters contained in the water.

The combustion of this residue and the remaining parts of the process are conducted precisely in the manner prescribed by Frankland. The residue is mixed with oxide of copper and transferred to a narrow combustion tube closed at one end, the tube filled in with granular oxide of copper, a roll of bright copper gauze inserted, and the open end of the tube narrowed and drawn out before the blowpipe. The tube thus prepared is laid in the combustion furnace, and connected by air-tight joints to a Sprengel pump, by means of which it is exhausted of air. It is then heated to redness, care being taken that the anterior part of the tube containing the copper and granular oxide, is red-hot before heat is applied to that portion containing the water residue. The gas produced by this combustion is pumped out into a tube standing in the mercury at the outfall of the Sprengel pump, and is transferred from thence into a suitable apparatus, in which it can be measured and analysed, and the amounts of carbonic acid and nitrogen it contains determined. From these data the quantities of organic carbon and nitrogen in the water are ascertained by a simple calculation. The amount of nitrogen here obtained requires no correction on account of the ammoniacal compounds pre-existing in the water, as it would in Frankland's method.

I have employed the foregoing process with complete success in the analysis of numerous specimens of water, with nitrates ranging from 5 to 0·5 parts NO_3 in 100,000, and have found the results given by it approximate very closely to those obtained by the sulphurous acid method, at least in the case of the few waters examined. The number of comparative observations I have made is too limited to serve as conclusive evidence of the accuracy of this process, or of the general concordance or discordance of its results with those obtained by Frankland's method. They were all made upon the same class of waters, which contained very little organic matter, and although they showed a close agreement, they might only be misleading if quoted here alone.

In practice the process here described effects a great saving in time, besides being less troublesome than that now employed, and comparatively free from objection on the score of its destructive action on the organic matter. In Frankland's process, the water is kept in contact with sulphurous acid at a high temperature for upwards of 24 hours, while in this, the distillation and evaporation together do not occupy more than three, or at most four hours, and during the greater part of

this time there is no acid present to cause any destruction. It is true that the digestion of the water with the copper-zinc couple may occupy a considerable time, but it requires no attention, and since metallic zinc and copper have not the least destructive or corrosive action on the organic matter in water, the duration of the digestion cannot be counted as an objection upon chemical grounds. Moreover, the estimation of the nitric acid is accomplished in the same operation, and the digestion would be necessary for this purpose alone. The process, therefore, is not only free from the sources of error which accompany the use of sulphurous acid for destroying the nitrates, but is more rapid than Frankland's; and since it permits the analyst to ascertain by direct tests, that the nitric acid is wholly converted into ammonia prior to distillation, it gives him greater confidence in the results of his analysis, as regards both the nitric acid and the organic nitrogen.

XXVII.—*On a New Theory of the Conversion of Bar-iron into Steel by the Cementation Process.*

By R. Sydney Marsden, D.Sc., F.R.S.E., F.C.S.

It is a well-known fact that when bar-iron is laid in alternate layers with charcoal powder in a converting furnace, and exposed to a temperature of or a little above a red heat, the carbon finds its way into the interior of the bar of iron, and that in this way steel is produced. This process, which takes many days for its completion, varying from seven to ten or eleven, is known by the name of the *Cementation process*.

The manner in which the carbon finds its way into the interior of the bar of iron is an anomalous operation (the only one of its kind presented in chemistry) which has never received any satisfactory explanation.

To account for this extraordinary change three different theories have been propounded, which may be briefly summarised as follows:—

1. *The Occlusion of Gases Theory.*

This theory is the one which is generally accepted as the most probable explanation of the subject. It was originally proposed by Leplay (Gay-Lussac, *Ann. de Chim. et de Phys.*, 1846), and supposes the conversion of the iron into steel to be due entirely to the action of carbonic oxide.

The oxygen of the air originally interposed between the particles of the carbon is converted into carbonic oxide, which is absorbed into the pores of the bar by the occlusive power of the iron, and is there robbed of half its carbon by the metal, and converted into carbonic acid. The carbonic acid then diffuses out of the bar again, and coming in contact with more carbon is again transformed into carbonic oxide, which being once more occluded into the iron, is again robbed of part of its carbon, and so on, the carbonic oxide, as it were, playing in this way the part of a carrier of carbon into the interior of the iron bar.

The second theory, known as

2. *The Combination Theory,*

may be thus shortly stated.

The outermost layer of the iron bar in contact with the solid carbon is supposed to combine with it, and thus form a carbide of iron. The carbide of iron thus produced and forming the outermost layer, is then supposed to give up its carbon to the layer of iron next to it, which in its turn gives it up to the layer next to it, and so on, until the carbon finds its way into the interior of the bar. The outermost layer then again combines with another quantity of carbon, which is again handed on as before, until the whole bar throughout becomes completely carburised. Professor Percy says: "In this theory it is easy to understand how the outermost layer of the metal should become carburised, but not easy to understand why this should give up carbon to the layer immediately underneath, the second layer to the third, and so on in succession, until the centre of the bar of iron, even though of considerable thickness, receives its full complement of this element: a continual addition of carbon from without supplying the deficiency, as layer after layer in turn parts with carbon" (Percy's *Iron and Steel*, vol. ii, p. 110, 1864). If we admit that there is chemical combination, a point on which I myself am very doubtful, why should one layer yield up its carbon to another?

3. *The Theory of Solution.*

On this theory the same author remarks: "If this phenomenon is analogous to solution, it appears somewhat more intelligible; for although the iron is not in a state of fusion, yet it is strongly heated, and its particles have thereby acquired a sensible degree of freedom of motion" (*ibid.*). Although this theory would render the subject more intelligible, still it is most improbable, for before the carbon could be dissolved or mechanically carried in, in the manner suggested by this theory, convection currents would require to be distinctly set up, such as could not be obtained unless the iron were in a molten condition.

4. *A New "Theory of Diffusion."*

In a paper on "The Diffusion of an Impalpable Powder into a Solid Body" (*Proceedings Royal Society Edin.*, **10**, 712) I have shown that when amorphous carbon in an impalpable powder is kept in contact with porcelain at a temperature considerably above redness, but not sufficient for the latter to become fused, the carbon will, if left for a number of hours, diffuse into the porcelain, and ultimately permeate it throughout.

This, then, it is evident (as remarked in that paper) is an analogous case to, and shows us precisely what takes place in, the conversion of bar-iron into steel by the "cementation process."

The carbon in the state of an impalpable powder *diffuses* into the bars of iron whilst they are in an expanded and softened state, the operation taking from seven to ten days before it is completed. Thus it seems to me to explain in a simple manner the hitherto unsettled question of the conversion of iron into steel by the cementation process, and to render unnecessary the "Occlusion of Gases" theory.

An objection might perhaps be raised to this theory on the ground that in my former experiments there is no proof that the carbon said to have diffused into the porcelain was not due to the reaction of iron compounds in the porcelain, as it is known that ferruginous bricks exposed to gases containing CO cause a deposition of solid carbon in their interior in virtue of Bell's reaction.

The porcelain in which these phenomena were observed consisted of Berlin porcelain crucibles. Now the amount of iron in these crucibles is excessively small (not at all comparable with ferruginous bricks), and certainly not sufficient to account for the presence of carbon in such large quantity (as was actually the case) by the above-mentioned theory of its decomposing action in CO; besides I can hardly think that carbon deposited in such a way would be in particles of sufficient size to render them distinctly visible by the microscope. Again, in the experiments it was found that the carbon was present in the largest proportion in the glaze of the crucible (which certainly contained no iron), and the parts nearest to the carbon. For my own part, I am fully convinced that the carbon entered the crucible by a process of diffusion, and if even it were found that porcelain exposed to an atmosphere of CO had carbon deposited in its interior, I do not see that that would prove diffusion had not also taken place in these experiments.

The fact that carbon can be extracted from, as well as introduced into, solid iron by a process of cementation, seems to favour this "Theory of Diffusion," and to show that the carbon in converted bar is not in a state of combination with the iron as required by the

occlusion and combination theories, but merely present in an extremely finely divided amorphous condition.

Professor Percy says, "When cast-iron is imbedded in the powder of red hæmatite, and kept at a bright red heat during two or three days, it loses carbon, acquires a considerable degree of malleability, and is converted into what is termed malleable cast-iron."

Dr. W. A. Miller has published the following analyses of the metal before and after the process:—

	Before.	After.
Specific gravity	7·684	7·718
Carbon { combined.. 2·217 / uncombined 0·583 } ..	2·800 { 0·434 / 0·446 }	0·880
Silicon	0·951	0·409
Aluminium	trace	trace
Sulphur.....	0·015	0·000
Phosphorus	trace	trace
Sand	0·502	—

Hence about four-fifths of the combined carbon appears to have been removed, while the uncombined or graphitic carbon suffered scarcely any diminution. The abstraction of more than half the silicon seems very remarkable, and I cannot in the least understand it. I have spoken to Dr. Miller on the subject, and he assures me that there is no reason to question the accuracy of the result. (Percy, *Iron and Steel*, p. 110, 1864.)

The above experiments of Professor Miller would appear to confirm my views.

The carbon present in the iron bar in an impalpable amorphous condition (on the supposition that the carbon is not in combination with the iron) is able again to diffuse out of the pores of the metal in the same way as it diffused into it, but the scales of graphitic carbon being of too great dimensions to pass through the pores of the iron, and thus diffuse out, are retained; still some slight portion of the graphite might be sufficiently small to do this, which would account for the slight difference indicated in the analysis.

XXVIII.—*Researches on the Relation between the Molecular Structure of Carbon Compounds, and their Absorption Spectra.*

By W. N. Hartley, F.R.S., &c., Professor of Chemistry, Royal College of Science, Dublin.

I. *General Conclusions as to the Actinic Absorption exerted by various Carbon Compounds.*

It has already been shown by former experiments, in the performance of which Professor A. K. Huntington was associated with me (*Phil. Trans.*, Part I, 1879): 1st. That every increment of CH_2 in a homologous series of alcohols and of acids effects an absorption of the more refrangible of the ultra-violet rays, so that the greater the number of carbon-atoms in the molecule, the shorter is the transmitted spectrum. 2nd. That the terpenes with the composition $C_{10}H_{16}$ possess in a high degree the power of absorbing the ultra-violet rays of the spectrum, though they are inferior in this respect to benzene and its derivatives. Terpenes with the composition $C_{15}H_{24}$ have a greatly increased absorptive power, as shown by the greater extent to which they suffer dilution with a transparent solvent before the transmission of all rays is attained. 3rd. That benzene and its derivatives, in addition to abnormally great absorptive power, show the peculiarity of *absorption-bands* when dilute solutions are examined.

On reviewing these facts, and considering the large number and varied character of the substances examined, many of which have not been even mentioned in previously published papers, the conclusion seemed inevitable that banded spectra are caused by such a compact molecular structure as chemists attribute to the double linking of three pairs of carbon-atoms in a closed chain. It appeared to me to be very desirable to ascertain exactly the effect of various atomic groupings upon the absorption of the ultra-violet rays.

II. *The Absorption shown by Certain Bodies constructed on an Open Chain of Carbon-atoms.*

The first question that called for solution was, whether bodies supposed to contain two doubly-linked adjacent carbon-atoms exhibit any peculiarities in their absorption-spectra? To decide this point, ethylene, amylene, and allyl alcohol were selected for examination.

Ethylene Gas.—A collimator tube 36 inches long was filled with the

pure gas, the pressure at the time being 760 mm., and the temperature 14° C. A quartz lens closed one end of the tube, the other end near the slit was closed by a cap of quartz. A tube at the end of the collimator, farthest from the slit, was attached at right angles and furnished with a **T**-tube with three taps upon it, one serving to close the connection between the tube and an air-pump, another attached to the tube proceeding from the reservoir of gas, and the third fixed to the collimator tube. It was found, however, in practice that the tube could be filled by simple displacement of air instead of by the more troublesome method of exhaustion and replacement.

Very little absorption was noticed as being caused by ethylene; it weakens the extremely refrangible rays in much the same way that methylic alcohol does.

Amylene.—A quantity of this liquid carefully rectified had a boiling point varying between 28° and 37°.

Three different fractions of this liquid were examined in the manner already described in the accounts of experiments on aromatic compounds and essential oils. The liquids were undiluted and diluted with pure alcohol in such proportions that the amylene formed $\frac{1}{10}$th, $\frac{1}{20}$th, $\frac{1}{50}$th, $\frac{1}{100}$th, $\frac{1}{500}$th, and $\frac{1}{1000}$th of the volume of the six different solutions of each fraction.

The undiluted liquids as one could foresee caused considerable absorption as far as the line Cd 17 wave-length = 274·34 (Mascart). No intermediate absorption was in any case revealed on diluting the liquids.

Allyl Alcohol.—A pure specimen of this substance boiling at 97° was photographed before and after dilution. Solutions in pure ethylic alcohol containing $\frac{1}{10}$th, $\frac{1}{50}$th, and $\frac{1}{100}$th of their volume of the pure substance were particularly examined, but no absorption-bands were seen.

Many careful observations have been made on isomeric alcohols, secondary and tertiary, as for instance, isopropylic, isobutylic, two amylic alcohols with different boiling points, iso-octylic alcohol, and trimethyl carbinol. No absorption-bands were noticed in any case.

To ascertain the effect of what is termed the treble-linking of two carbon-atoms, acetylene was chosen, first, because it is the simplest and most easily prepared of such bodies; and secondly, because its easy conversion into benzene shows it to be nearly related to that substance.

As in the case of ethylene, the collimator tube was filled with the gas at a pressure of 760 mm., and a temperature of 14°. The tube held 450 c.c. or little more than half a gram weight of the body. The acetylene was prepared from cuprous acetylide by the action of hydrochloric acid. An absorption of the extreme rays extending only as far

as the line Cd 23, wave-length = 231·83 (Mascart), was noticed, but no bands were visible. This is strikingly different from the behaviour of benzene, for half a gram of substance exerts only a slight absorption at the extremity of the spectrum, while 5 mgrms. of benzene or even less would show several well-defined absorption-bands.

Taking into consideration an immense number of observations on various bodies, it appears that in all cases where the carbon-atoms are supposed to be arranged in an open chain, no absorption-bands are seen.

In no carbon compound whatever has the arrangement of the hydrogen and oxygen-atoms been identified with the occurrence of the absorption-bands.

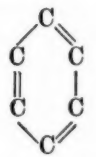
The replacement of hydrogen in any compound by the radicals of the formulæ C_nH_{2n-1}, by NH_2, by OH, by COOH, or SO_3H, has no influence on the production of absorption-bands.

When the halogens are substituted for hydrogen in a compound, and the result is a colourless body, no bands are caused to appear in the spectrum. This was proved by the examination of ethyl chloride, ethylene dichloride, chloroform, carbon tetrachloride, and other substances.

III. *On the Nature of the Actinic Absorption exerted by various Closed Chains of Carbon-atoms.*

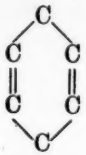
With hydrocarbons containing at least 6 atoms of carbon and their derivatives, there are four possible arrangements of a symmetrical character, which admit of the carbon-atoms forming a closed chain.

1st. Three pairs of carbon-atoms may be doubly-linked together, as according to Kekulé's theory we assume is the case in aromatic compounds generally.

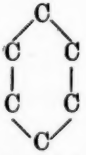


2nd. Each carbon-atom may be directly combined with three other carbons, as in Ladenburg's prism formula, in which each solid angle of a prism represents a carbon-atom, the three edges constituting the angle being the three combining powers of the atom which are saturated by carbon only. See also Körner's view of the constitution of benzene and its derivatives (*Chem. Soc. J.*, **29**, 204).

3rd. Two pairs of carbon-atoms may be doubly-linked together as is generally assumed to be the case in turpentine oil.



4th. The six carbon-atoms may be singly united with each other, as in benzene hexachloride.



All compounds, the nature of which accords with the first arrangement, are so constituted that their structure should be perfectly well represented by the second formula.* Such substances show absorption-bands in the spectra transmitted by dilute solutions.

When the hydrogen atoms in benzene are replaced by alcohol-radicals, or by the groups OH, NH_2, COOH, or NO_2, the absorption-bands do not disappear, they are only modified, the modification being generally, 1st, a fusion of several narrow bands into one broad band; 2nd, an increase in the intensity of the absorption, so that the bands are still visible in photographs of the spectra transmitted by much more dilute solutions.

Evidence of this is gathered from examinations of the spectra transmitted by benzene, ethyl-benzene, trimethyl-benzene, phenol, pyrogallol, aniline, and phthalic acid, ortho- and para-toluidine, benzoic acid, and the three hydroxybenzoic acids, nitro-benzene, ortho-nitrophenol, para-nitrophenol, meta-nitraniline, and para-nitraniline (see Diagrams Nos. 6 to 27, *Phil. Trans.*, Part I, 1879).

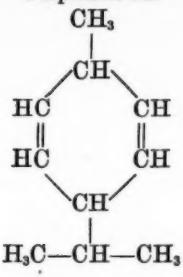
In the glucosides, salicin and phlorizin, it is the benzene-residues which cause the spectra to be banded, for glucose shows no such action.

The presence of absorption-bands in the ultra-violet spectra transmitted by compounds of the aromatic series, is due to the particular arrangement of the six carbon-atoms, forming the nucleus of the molecules of such compounds.

There are good reasons for believing that oil of turpentine has two pairs of carbon-atoms doubly linked, and that a closed chain including these two pairs of atoms forms the nucleus of this substance (see Schorlemmer's *Chemistry of Carbon Compounds*, p. 300; also Watts's *Organic Chemistry*, p. 596, &c.).

* Dr. Japp has pointed out that Koerner's formula is inadmissible, and that Ladenburg's formula is not capable of such adjustment as to express the constitution of naphthalene and phenanthrene (*Chem. Soc. J.*, **37**, 89 [1880]. See also Armstrong and Groves' edition of Miller's *Organic Chemistry* (p. 1003).

Turpentine oil.



It has not been decided whether this arrangement of the carbon-atoms, forming the nucleus of the compound, may be assumed to represent the internal structure of all terpenes with the composition $C_{10}H_{16}$. There can be little doubt, however, about their structure being similar, because of their similarity in physical and chemical properties.

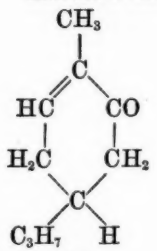
The so-called "terebene" has been shown by Drs. Armstrong and Tilden to be an impure camphene containing the hydrocarbons cymene and terpilene (*Chem. Soc. J.*, **34**, 757, 1879). The sample received from Dr. Tilden contained no cymene.

The result of the examination of about 50 essential oils has already shown that the terpenes, when pure, including oil of turpentine and "terebene," exert no selective absorption on the rays of the ultra-violet spectrum. Hence, assuming the terpenes to have a nucleus of carbon-atoms in accordance with the third arrangement, it follows that:

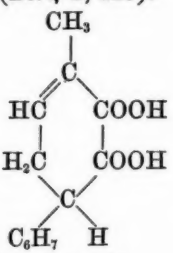
A closed chain of carbon-atoms in which only two pairs of contiguous carbons are doubly linked does not give rise to absorption-bands.

Now come the consideration of such bodies as contain 6 carbon-atoms singly linked. Whatever formula may best represent the constitution of camphor, the researches of Kekulé, Hlasiwetz, Kachler, and Wreden at any rate favour the assumption that it is founded on a closed chain of carbon-atoms. Oppenheim's researches show that,

Kekulé's formulæ (*Ber.*, **6**, 929).

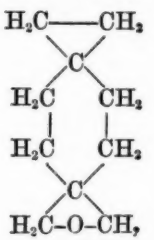


Camphor.



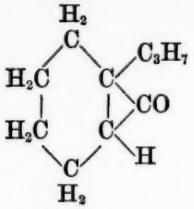
Camphoric acid.

Hlasiwetz's formula (*Ber.*, **3**, 539).

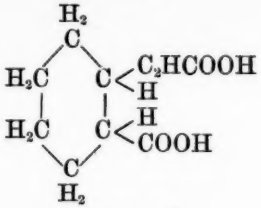


Camphor.

Kachler's formulæ (*Annalen*, **169**, 185).

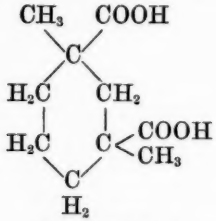


Camphor.



Camphoric acid.

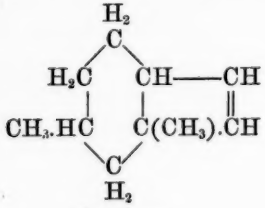
Wreden's formula (*Annalen*, **163**, 323).



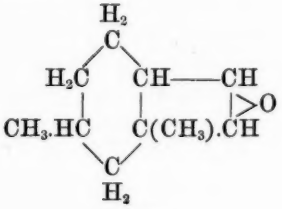
Camphoric acid.

from the ease with which camphor is converted into cymene, and cymene into camphor, six of the carbons in this compound form a closed chain, or nucleus, the four remaining carbons being disposed of as side-chains (*Ber.*, **5**, 631).

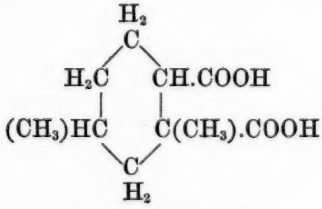
According to Dr. H. E. Armstrong camphene, camphor, and camphoric acid are related to each other in the manner indicated by the following formulæ (*Chem. Soc. J.*, **35**, 757, 1879).



Camphene.



Camphor.



Camphoric acid.

The evidence of chemical reactions from which all the above formulæ are derived, is distinctly in favour of camphor being formed on a nucleus consisting of a closed chain of six singly-linked carbon-atoms. It has already been stated that side-chains do not affect the absorption-spectra except by increasing the intensity of the bands exhibited by aromatic compounds; and on this account the nature of the side-chains entering into the molecule of camphor and camphoric acid may be omitted from present consideration. Any one of the above graphic representations of their molecules would accord with camphor and camphoric acid, being substances of a more diactinic character than either benzene-derivatives or terpenes: for notwithstanding that camphor has the same number of carbon and hydrogen atoms in the molecule as oil of turpentine, still the carbons are not so compactly united. This we know to be the case from its specific refractive energy being less than that of the terpenes. Specimens of camphor oil, camphor, and camphoric acid were examined to ascertain whether or not these substances behaved like benzene-derivatives, that is to say, with bodies containing three pairs of doubly-linked carbon-atoms.

Camphor oil.—This specimen was kindly lent by Dr. Gladstone. A portion boiling between 170° and 180° diluted to various degrees up to 500 and 1000 times its volume of alcohol, showed no absorption-bands and no great absorptive power.

Camphor.—Several specimens of camphor were examined.

No. 1. Crystals of camphor which had separated from camphor oil with a high boiling point lying between 200° and 220°.

No. 2. An ordinary specimen of commercial camphor resublimed.

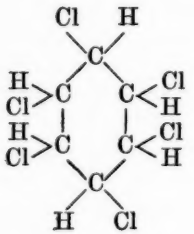
No. 3. Fine crystals of camphor spontaneously sublimed in a specimen bottle.

The specimens Nos. 1 and 2 exhibited absorption-bands, which, however, on account of their feeble character and the ease with which dilution caused them to disappear, were evidently due to the presence of some impurity. No. 3 transmitted a perfectly continuous spectrum, and was in fact so transparent that a solution containing $\frac{1}{500}$th of the substance transmitted all rays less refrangible than Cd 25. This far exceeds in diactinic quality the numerous specimens of terpenes I have examined.

Camphoric Acid.—A well crystallised specimen of this substance was obtained from Mr. Kahlbaum's agents. It was dissolved in alcohol and solutions containing the following fractional proportions of the substance were examined, viz., $\frac{1}{10}$th, $\frac{1}{25}$th, $\frac{1}{50}$th, $\frac{1}{100}$th and $\frac{1}{150}$th. None of these solutions showed any absorption-bands, and they proved the transparency of this substance to be much greater than that of benzene and the terpenes, since a solution containing 1 part of camphoric acid in 150 parts of alcohol transmitted all rays

extending to a little beyond Cd 18. It will be noticed that the transparency of the substance is not quite so great as that of camphor, and this is exactly what could be foreseen, because the group COOH always increases the amount of absorption, and it occurs twice in the molecule of camphoric acid. Camphor oil is probably a terpene. Solid camphor is a substance differing in its specific refractive energy, and particularly in its actinic transparency, from the terpenes and their oxidised derivatives, inasmuch as in comparison with these bodies it is unusually diactinic. Indeed the high transparency of camphor compared with its molecular weight is consistent only with either an open chain, or with a singly-linked closed chain of carbon-atoms.

A typical example of a body containing six carbon-atoms singly linked in a closed chain is the substance known as benzene hexchloride. The usual graphic representation of the substance is the following:—



Reasoning on the results obtained from the examination of camphor, camphoric acid, and the terpenes, and the evidence afforded by chemical reactions of the constitution of these bodies, I felt convinced that benzene hexchloride would yield spectra characterised by great transparency and freedom from absorption-bands. In fact the examination of this substance was regarded as the crucial test of the correctness of my previous deductions.

Benzene Hexchloride.—A sample of this body was carefully prepared from a pure sample of benzene by passing a stream of chlorine through the boiling liquid. The crystalline product was purified by washing with alcohol and recrystallising from the same liquid. Solutions in alcohol containing $\frac{1}{50}$th, $\frac{1}{100}$th, $\frac{1}{200}$th, $\frac{1}{300}$th, $\frac{1}{400}$th, $\frac{1}{500}$th of their weight of the body were examined. In no case were absorption-bands visible even when three cells full of liquid, equivalent to a thickness of 45 mm., were examined. The solution containing as much as 1 per cent. of benzene hexchloride transmitted all rays a little less refrangible than Cd 23, and this great transparency was but slightly impaired by increasing the number of cells of liquid from one to three. Considering its high molecular weight this is a substance of most remarkable transparency.

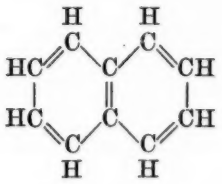
It is evident that there is an essential difference between substances containing a carbon-nucleus constituted like that of benzene and bodies such as camphor, benzene hexchloride, and the terpenes. It has been shown quite recently by Julius Thomsen (*Ber.*, **13**, 1808 [1880]) that the heat of combustion of benzene, if the carbons are linked as in Kekulé's formula, would amount to 846,040 heat-units, whereas if there are nine single linkings in the molecule it would be 802,330 units. The experimental number obtained by Thomsen was found to be 805,800: hence he concludes that the six carbon-atoms in benzene are nine times singly linked with each other. Subject to the correctness of this deduction, I consider the following conclusion to be established:—

No molecular arrangement of carbon-atoms causes selective absorption unless each carbon is itself united to other three carbon-atoms, as in the case of benzene.

IV. *On the Absorption Spectra of Condensed Benzene Nuclei.*

The results of the examination of naphthalene and anthracene with their derivatives was awaited with much interest, because judging from observations made on a large number of benzene-derivatives, and having regard to the generally accepted views of the constitution of naphthalene and anthracene, it was expected that the spectra transmitted by these substances would show a larger number of absorption-bands, and that the bands would be of greater intensity than in the case of benzene. Actual experiment has to some extent satisfied these anticipations.

Naphthalene.—The constitution of naphthalene may be represented by the fusion of two benzene-nuclei, as shown in the accompanying graphic formula proposed by Erlenmeyer and confirmed by Græbe, which for the present I shall adopt.



A perfectly pure specimen of this substance, which had been prepared with great care, analysed and found to yield theoretically correct proportions of carbon and hydrogen, and known to possess the correct melting point and boiling point, was examined. Solutions in alcohol

were prepared containing $\frac{1}{1000}$th, $\frac{1}{2000}$th, $\frac{1}{3000}$th, $\frac{1}{4000}$th, $\frac{1}{5000}$th, $\frac{1}{6000}$th, $\frac{1}{10000}$th, $\frac{1}{20000}$th, $\frac{1}{50000}$th, $\frac{1}{60000}$th, $\frac{1}{80000}$th, $\frac{1}{90000}$th, and $\frac{1}{100000}$th of their weight of the substance. With solutions containing 1 in 10,000 the rays are transmitted as far as a position lying halfway between the line Cd 12 and Cd 17.

Solutions containing $\frac{1}{30000}$th show four well-defined bands of absorption between 12 and 18 Cd, and these continue strongly marked in a solution containing $\frac{1}{80000}$th, while those of the bands are seen in solutions containing smaller proportions even than $\frac{1}{100000}$th.

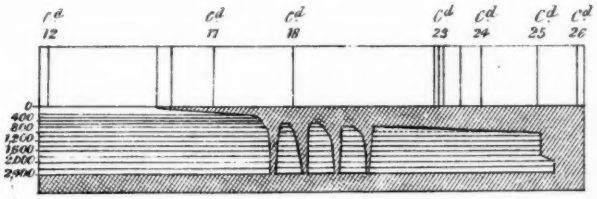
No idea of the nature of the actinic absorption can be conveyed without the aid of diagrams. The accompanying illustrations were each drawn from a series of photographs taken from spectra transmitted by solutions of various strengths. By taking the proportions of substances in the various solutions examined as ordinates, and the positions of the absorption-bands as abscissæ, the position of these bands being referred to a photograph of the lines of cadmium of known wave-length, a series of representations is obtained of the relative intensities of the absorptions and the positions of the absorbed rays. In order, however, that a proper comparison might be made of the *intensity* of the absorption-bands of different substances, it would of course be necessary to draw the ordinates of the curves in every case of the same dimensions. This has been altogether quite impossible; but it will be noticed that some sort of comparison may be made, since when the ordinates represent not more than 20,000 parts of liquid as containing 1 part by weight of the substance, they are drawn to the scale of 4,000 parts to the inch, larger proportions, in which as many as 100,000 parts of solution may contain 1 part of the substance, are represented by 40,000 parts to the inch.* A special series of fourteen photographs of benzene was taken, and a diagram was made from them. (Diagram No. 1.) This diagram differs somewhat from the diagram in the *Philosophical Transactions*, Part I, 1879. In the first place the drawing is made on a different scale, which is at once evident, and, secondly, the photographs differ from the previous series in the following particulars: they are made from solutions containing parts by weight of benzene in weighed proportions of alcohol instead of from solutions, diluted volume for volume. Then the dispersion of the more refrangible rays is less than in the former experiments, so that certain weaker bands are not reproduced here. The latter remark applies also to a second series of photographs taken from solutions of anthracene, which will be mentioned later on.

Anthracene.—Anthracene is considered to have a structure repre-

* In reproduction the drawings have been reduced to three-fifths of their original size.

DIAGRAM I.

BENZENE C_6 H_6 B.P. 80·5.



Scale. 4,000 parts to $\frac{3}{8}$ths of an inch.

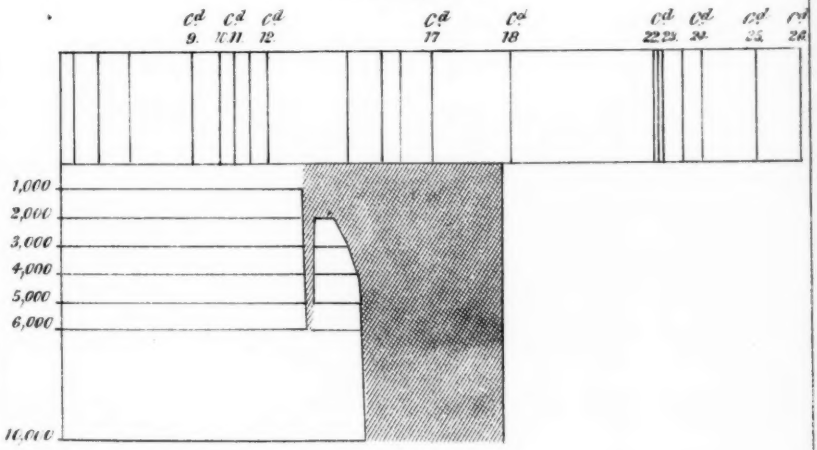
The Ordinates = proportion of alcohol by weight to one part by weight of Benzene.

Thickness of layer of liquid = 0·61 inch or 15mm.

DIAGRAM II.

NAPHTHALENE.

Numbers indicating the position of cadmium lines of known wave length.



Scale. 4,000 parts to $\frac{3}{8}$ths of an inch.

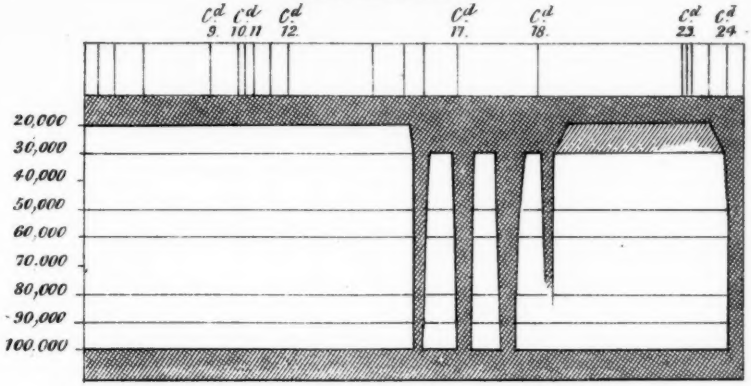
The Ordinates = parts of liquid containing one part by weight of Naphthalene.

Thickness of layer of liquid = 15 mm

Harrison & Sons, [illegible]

Diagram III.

NAPHTHALENE.

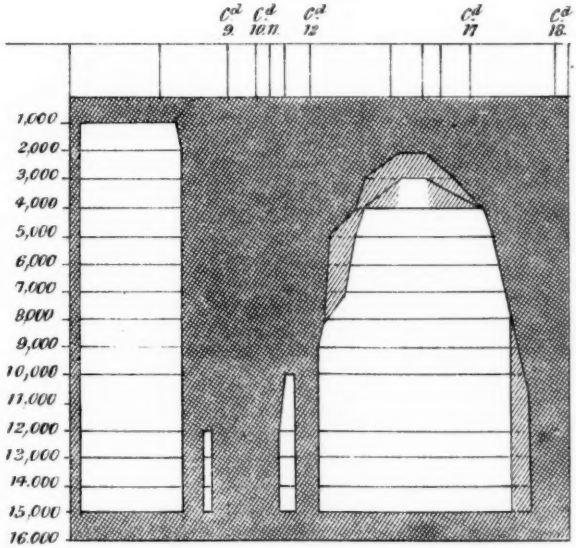


Scale. 40,000 parts to $\frac{3}{5}$ths of an inch.

The Ordinates = parts of liquid containing one part by weight of Naphthalene.

Diagram IV.

ANTHRACENE.



Scale. 4,000 parts to $\frac{3}{5}$ths of an inch.

The Ordinates = the proportions of alcohol containing one part by weight of Anthracene.

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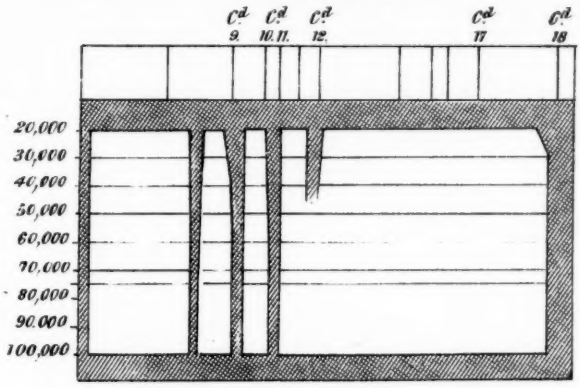
Diagram V.

ANTHRACENE.

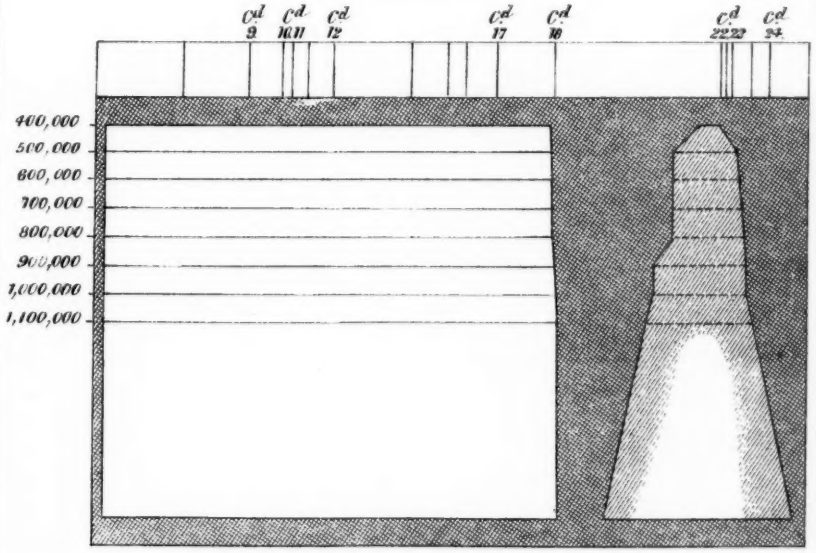


Scale. 40,000 parts to $\frac{1}{5}$ths of an inch.

The Ordinates = the proportions of alcohol containing one part by weight of Anthracene.

Diagram VI

ANTHRACENE.



Scale. 400,000 parts to $\frac{2}{5}$th of an inch.

The Ordinates = the proportions of alcohol containing one part by weight of Anthracene.

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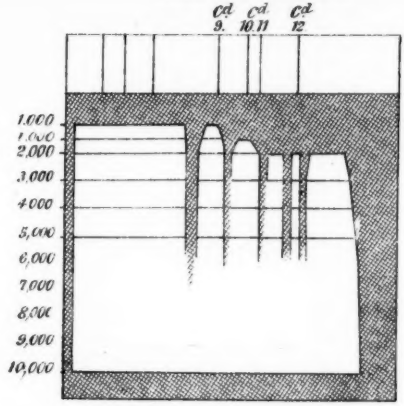
DIAGRAM VII.

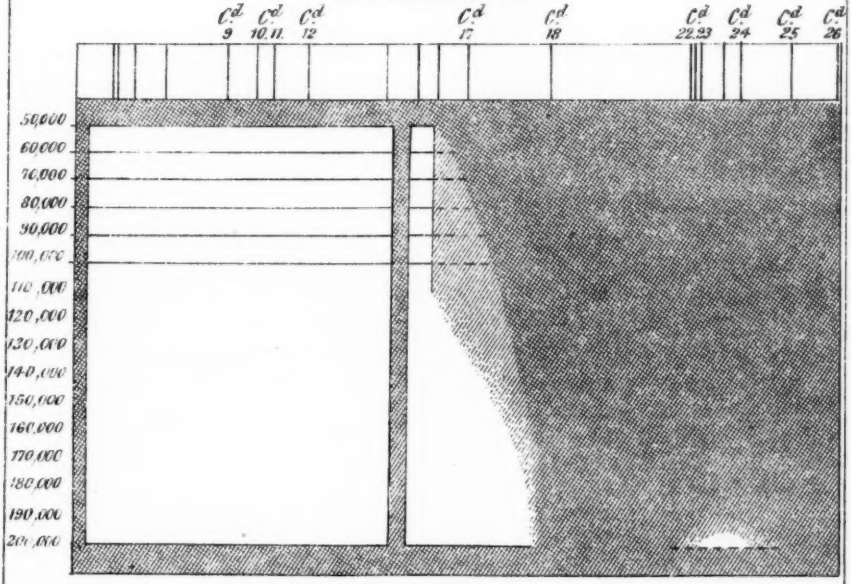
PHENANTHRENE.



Scale. 4,000 parts to $\frac{3}{8}$ths of an inch.

DIAGRAM VIII.

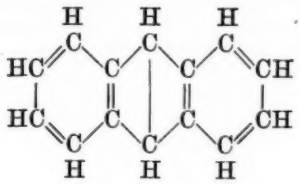
PHENANTHRENE.



Scale. 40,000 parts to $\frac{3}{8}$ths of an inch.

Harrison, Printer, 59 Maiden Lane, W.C.

sented by the formula proposed by Bahr and Van Dorp (*Ber.*, **7**, 16). It may be considered as derived from three benzene-nuclei, the carbons of which are disposed as in the accompanying figure :—



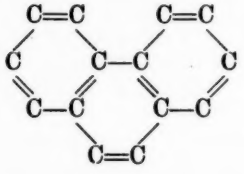
The specimen examined was a remarkably pure one, given me by Mr. W. H. Perkin. It was in large crystals, exhibiting a beautiful blue fluorescence. Solutions were prepared both with acid and absolute alcohol, but no difference was observed in the spectra of the two solutions in various stages of dilutions. Two sets of diagrams were drawn, one of which accompanies this paper; they were each made from solutions prepared with glacial acetic acid and diluted with absolute alcohol. I need scarcely say that the absolute purity of the alcohol and acid was tested by taking their photographic spectra before use. The photographs taken for the latter series were thirty-nine in number, the details of the strength of the different solutions are the following :—There was 1 part of anthracene by weight in the following proportions of liquid : 1,000, 2,000, 3,000, 4,000, 5,000, 6,000, 7,000, 8,000, 9,000, 10,000, 12,000, 14,000, 15,000, 20,000, 30,000, 40,000, 50,000, 60,000, 70,000, 75,000, 100,000, 200,000, 300,000, 400,000, 500,000, 600,000, 700,000, 800,000, 900,000, 1,000,000, 2,000,000, 3,000,000, 4,000,000, 5,000,000, 10,000,000, 20,000,000 30,000,000, 40,000,000, and 50,000,000.

In the first series of photographs there was an absorption-band faintly visible in the most refrangible part of the spectrum near Cd 23, when a solution was examined containing only one part of anthracene in 50,000,000 of liquid. This was not seen in the latter series of experiments, but there was still a slight general absorption of the most refrangible rays with a solution of one in 20,000,000 of liquid. The most refrangible of the numerous absorption-bands shown by this substance was visible in solutions containing only one part in 5,000,000.

The first characteristic absorption is seen in solutions containing proportions varying between $\frac{1}{2000}$th and $\frac{1}{10000}$th, Diagram No. 4; the next most strongly marked and characteristic spectra are obtained from liquids containing more than $\frac{1}{10000}$th and less than $\frac{1}{200000}$th, Diagram No. 5. One band of a distinctive character is visible only in solutions containing less than $\frac{1}{400000}$th of their weight of the substance,

and it continues *plainly* visible till a dilution of one part in 2,000,000 is reached.

Phenanthrene.—This substance, from its synthetical mode of production and its chemical character, is supposed to be related to naphthalene in somewhat the same manner as the latter is to benzene, and its carbon-nucleus may be represented thus:—



The specimen examined was obtained from Mr. Kahlbaum's agents. It was recrystallised from alcohol, and solutions of the purified crystals were made with absolute alcohol. In all 24 photographs were taken of solutions containing $\frac{1}{1000}$th, $\frac{1}{1500}$th, $\frac{1}{2000}$th, $\frac{1}{3000}$th, $\frac{1}{4000}$th, $\frac{1}{4500}$th, $\frac{1}{5000}$th, $\frac{1}{10000}$th, $\frac{1}{20000}$th, $\frac{1}{30000}$th, $\frac{1}{40000}$th, $\frac{1}{50000}$th, $\frac{1}{60000}$th, $\frac{1}{70000}$th, $\frac{1}{80000}$th, $\frac{1}{90000}$th, $\frac{1}{100000}$th, $\frac{1}{200000}$th, $\frac{1}{300000}$th, $\frac{1}{400000}$th, $\frac{1}{500000}$th, $\frac{1}{600000}$th, $\frac{1}{1000000}$th, and $\frac{1}{2000000}$th of their weight of the substance. The most dilute solution yielding a distinct absorption-band contained $\frac{1}{600000}$th of phenanthrene. Characteristic spectra from which the diagram curves were drawn were seen in liquids containing various proportions of the substance lying between 1 in 1,000 and 1 in 10,000, also 1 in 50,000 and 1 in 200,000 parts of alcohol. Diagrams No. 7 and No. 8.

In the hydrocarbons benzene, naphthalene, anthracene, and phenanthrene, the most prominent feature common to all the spectra is the group of four strong absorption-bands, situated in the case of benzene in the most refrangible part of the spectrum, lowered in refrangibility to the central portion in naphthalene, and still further reduced in phenanthrene and anthracene to the less refrangible rays.

In similar order the intensity of the absorption is enormously increased, being at least 40 times greater in the case of naphthalene than in benzene.

It is evident that there is a similarity of constitution in the carbon-nucleus of the bodies benzene, naphthalene, anthracene, and phenanthracene, as shown not only by their absorption-spectra, but by the methods of their synthetical production. It is undesirable to multiply the formulæ proposed for benzene, naphthalene, and anthracene; in order, however, to meet the requirements of all known facts, perhaps the single, double, and triple hexagons in common use are the most satisfactory graphic symbols, since they do not represent any particular view of the inner structure of the benzene nucleus.

V. *On the Cause of Absorption-bands in the Spectra transmitted by Benzene and its Derivatives.*

In the absorption of ultra-violet rays by hydrocarbons of the aromatic series we have two kinds of absorption made manifest, namely, a general absorption and a selective absorption. It is the selective absorption which distinguishes these from all other classes of carbon compounds. While the absorptive power of alcohols and fatty acids depends on and varies with the molecular weight of the compounds, or more strictly speaking with the number of carbon-atoms in the molecule, in aromatic compounds it entirely depends on the *structure of the molecule*. For instance, a terpene, $C_{10}H_{16}$, is much more strongly diactinic than naphthalene, $C_{10}H_8$, and benzene hexchloride, $C_6H_6Cl_6$, than benzene, C_6H_6. But it may be said that I propose to class benzene and naphthalene as bodies entirely differing in structure from the terpenes—camphor and benzene hexchloride. This is so, and I will therefore cite the case of cymene, $C_{10}H_{12}$, and naphthalene, $C_{10}H_8$; the latter is certainly more than five times greater in absorptive power than the former, and there is a similar difference between the isomeric bodies anthracene and phenanthrene, both with the composition $C_{12}H_{14}$. It may be observed in fact that such a difference is quite usual with isomerides of the aromatic series. (See Plates 22, 23, 24, 25, *Phil. Trans.*, Part I, 1879.)

When a molecule of a substance is capable of vibrating synchronously with a radiation the ray received on the substance is absorbed. The absorption is complete if the *direction* of vibration of the ray and of the molecule is the same, but the *phase* opposite. It is evident that general actinic absorption, exerted by carbon-compounds, is due to the vibration of the molecules, since absorption increases in extent with the number of carbon-atoms in the molecule, or in other words, the larger the molecule the lower the rate of its vibration. Selective absorption appears to be caused by the vibration of atoms within the molecule.

When a substance like benzene absorbs all rays more refrangible than the line 17 Cd, wave-length = 274·34 millionths of a millimetre, it is because the molecules are vibrating synchronously with these rays, and the number of molecules present is sufficient to damp all vibrations. When the liquid is diluted the number of molecules present is not sufficient to damp all the vibrations, and some rays are transmitted. If, however, certain carbon-atoms within the molecule are vibrating synchronously with certain rays, we shall have selective absorption of these rays after the general absorption has been so weakened by dilution as to allow them to pass. It is not possible to associate any of the absorption-bands of the substances hitherto

examined with any particular carbon-atoms, and I shall show presently that the atomic vibrations are dependent upon the vibration of the molecules. For the purposes of the present argument I have deduced the mean wave-length of the rays absorbed by the four principal bands in benzene, naphthalene, and anthracene. They are not considered to be more than rough approximations to the true measurements, for several circumstances prevent great exactitude, as for instance, the shading off of the bands on both sides or on one side more than another, the transference of the photographic impressions to paper, and the comparison of the diagram with a paper scale; but in order to give some idea of the care which has been taken in reading from the scale I append two or three sets of numbers obtained on different occasions by measuring the centres of the bands of absorption near their point of extinction.

Numbers approximately representing the Mean Wave-length of the Four Chief Bands of Rays Absorbed by Benzene, Naphthalene, and Anthracene.

Benzene—

261·6	254·8	249·7	244·7
261·3	254·9	249·7	244·6
—	254·7	—	—

Naphthalene—

285·5	272·6	263·1	255·0
285·5	272·5	263·1	254·5

Anthracene.—The least refrangible band of anthracene is not measurable on my scale of wave-length.

360·0	343·0	328·7
360·7	343·3	328·5
—	343·4	328·7

The mean of the numbers was taken for each substance, and from this mean wave-length and the velocity of light the mean rate of vibration of the molecules of benzene, naphthalene, and anthracene was calculated.

According to Fizeau the velocity of light is 315,364,000 metres per second.

Wave-length in millionths of a millimetre of the mean ray absorbed by benzene, naphthalene, and anthracene, and the rate of vibration per second of the molecules of these substances:—

	Mean λ.		Vibrations per second.
Benzene.....	252·6	=	1,248 billions.
Naphthalene....	268·7	=	1,177 „
Anthracene	343·9	=	910 „

The mean rate of vibration of the rays absorbed by naphthalene and anthracene is less than that of the rays absorbed by benzene. It follows from this that the bands in benzene, naphthalene, and anthracene, though conceived to be caused by the vibrations of the carbon-atoms within the molecule, are not independent of, but are a consequence of, the molecular vibrations; they must in fact be regarded as harmonics of the fundamental or molecular vibrations. When the rate of the fundamental vibration is reduced by the increase in size of the molecule the rate of vibration of the carbon-atoms is reduced in a similar ratio.

In the case of a vibrating string or tuning fork, greater amplitude of vibration means a louder note, in the case of a luminous radiation it means a brighter light; consequently the converse of this must hold good that a greater intensity of absorption is caused by a greater amplitude of vibration in the molecules of the absorbing medium, the number of atoms or molecules remaining constant. Hence it follows that as the absorbing power of naphthalene and anthracene is weight for weight greater than that of benzene, the amplitude of vibration of the molecules of these bodies is greater. Now the mean rate of vibration of the rays absorbed by naphthalene and anthracene is less than that of the rays absorbed by benzene, though the character of the absorption is the same in each case. Hence we may conclude that though the wave-form is the same or similar, the *amplitude* of vibration is greater, and the *rate* of vibration is slower. That the wave-form of these bodies is similar is due to the fact that naphthalene and anthracene vibrate as two benzenes, or rather as double benzenes. In this case, as the loudness of a note varies in the proportion of the square of the amplitude of vibration of a stretched string, it follows that we should expect the intensity of the absorption to be four times as great in naphthalene as in benzene, but in reality it is at least 40 times as strong.

The tone or quality of a note is characterised by its wave-form. The wave-form is subject to variations. 1st, according to the mode of producing the vibrations, and 2nd, according to the structure of the musical instrument.

Instruments of the same construction set in vibration in the same way will always evolve tones of the same quality or wave-form. Hence in the examination of molecular vibrations, as the same method of actuating the vibrations is always employed, the difference in wave-form must indicate a difference in structure, that is to say, in chemical constitution.

It is easy to predict from this that as the wave-form must manifest itself in a variety of absorption-bands, not only may we classify substances according to the spectra they transmit, but we may ascertain

their chemical constitution, and if the bodies in question be isomerides doubtless further researches will enable us at once to determine whether they be ortho-meta or para-derivatives.

As it is practically impossible to prepare the large number of organic bodies which are necessary for making an elaborate series of observations on the subject of isomerism, I venture to appeal to chemists who are in possession of pure preparations of isomeric substances of known constitution to forward small quantities to me for examination; a decigramme is generally amply sufficient, and frequently not more than a centigram of substance would be required.

XXIX.—*On Absorption-bands in the Visible Spectrum produced by certain Colourless Liquids.*

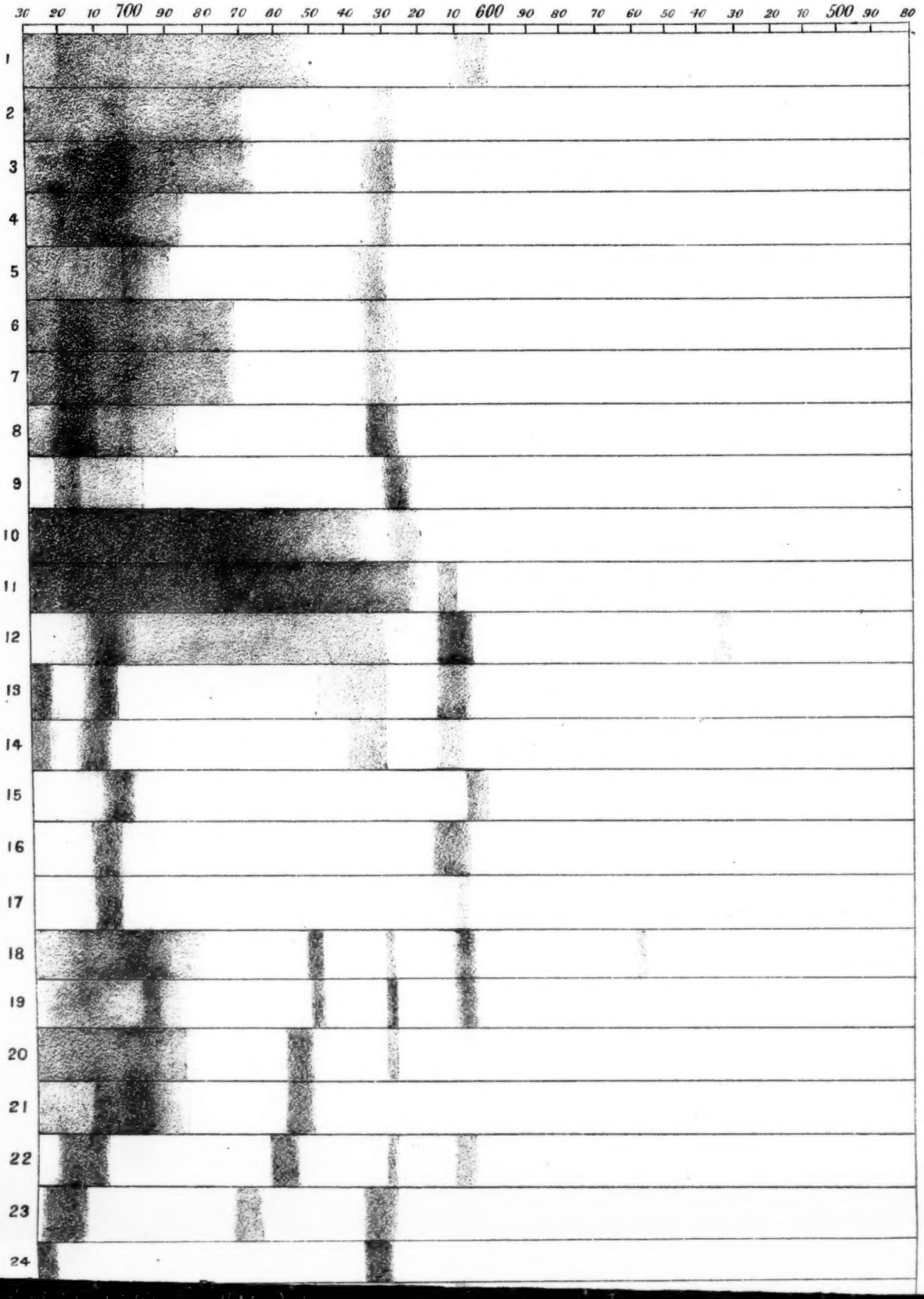
By W. J. Russell, Ph.D., F.R.S., and W. Lapraik, F.C.S.

In August last we published in *Nature* (vol. 22, p. 368, August 19th, 1880) a short statement of the results we had obtained by examining spectroscopically the light which had traversed considerable thicknesses of different colourless liquids, and we gave a diagram of the different visible absorption-bands produced. Since then we have extended and repeated our former observations.

The great advance made in this subject by the most important paper of Captain Abney and Colonel Festing on the absorption-bands in the infra-red end of the spectrum produced in colourless liquids, suggested our publishing in a connected form the results which we have obtained in the visible spectrum. All our observations are eye observations, made on columns of the liquids varying from 2 to 8 feet in length, and the spectroscope we used was one of Desaga's with a single heavy glass prism. The sources of light were a large argand burner, and the oxyhydrogen lime-light. In most instances both lights were tried, as it was found that with certain lengths and certain liquids, one light gave the best results, in the other case the other light.

In our communication to *Nature* we stated how we were led to this investigation, and how on examining a column of water 6 feet in length, we observed a distinct absorption-band. Its position is essentially between 600 and 610 (Fig. 1). The band is decidedly darkest on the more refrangible side, and ends sharply on that side, fading off far more gradually on the other side. When this band is

Plate I.


30 20 10 700 90 80 70 60 50 40 30 20 10 600 90 80 70 60 50 40 30 20 10 500 90 80
1 Water.
2 Methylic Alcohol.
3 Ethylic ,,
4 Propylic ,,
5 Amylic ,,
6 Amylic Iodide.
7 Amylene.
8 Ether.
9 Ethyl Iodide.
10 Aldehyde.
11 Acetic Acid.
12 Benzene.
13 Toluene.
14 Xylene.
15 Phenol.
16 Mono-chlor Benzene.
17 Di-chlor ,,
18 Ammonia in Water.
19 ,, Ether.
20 Methylamine in 6 ft.
21 ,, 4 ft.
22 Ethylamine.
23 Di-ethylamine.
24 Tri-ethylamine.

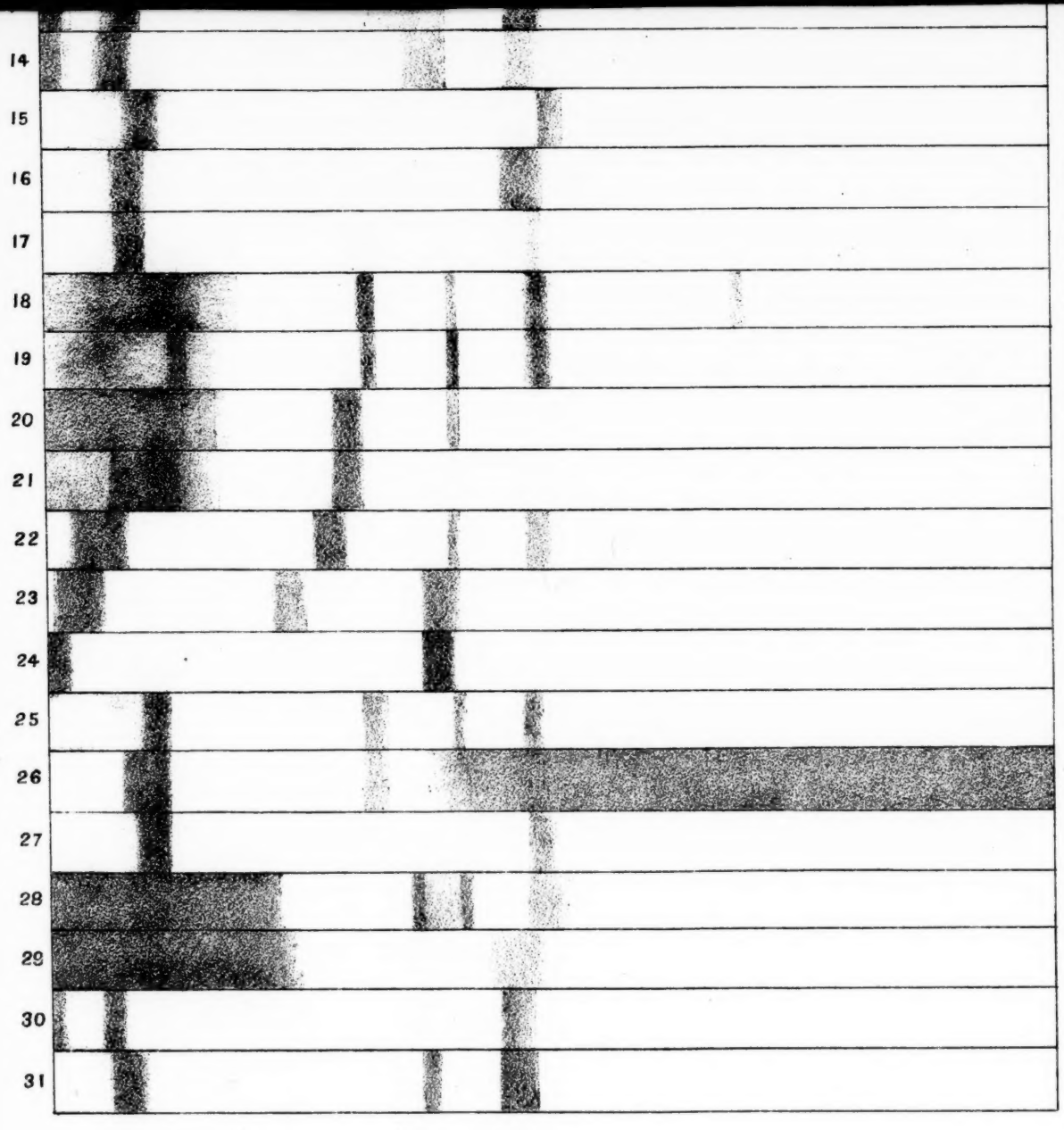
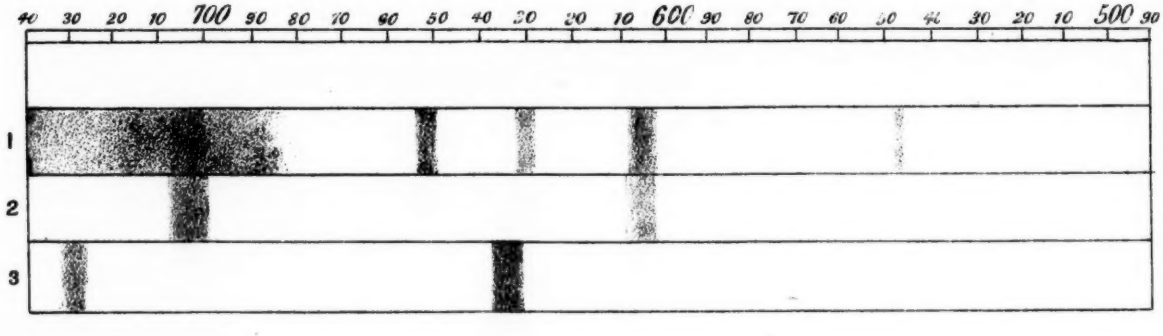


Plate II.



Harrison & Sons, Lith., St. Martins Lane, W.C.

distinctly visible, the general absorption in the red extends to about 655, and although too dark to allow us to speak with absolute certainty, we believe there is another band from about 705 to 723. We have also stated that on raising the temperature of the water from 20° to 60°, we saw no appreciable alteration in the intensity nor in the position of these bands, also whether ordinary or pure water was used, or even water saturated with ammonium chloride, or nitrate or carbonate, or potassium nitrate or lead nitrate or sodium chloride, or sugar, the intensity of this water-band was not altered. With a mixture of one volume of sulphuric acid and five volumes of water, it was also visible, but with ordinary pure commercial hydrochloric acid it required a column of 8 feet to see this band even faintly. Nitric acid (Fig. 29) gives a band visible in a column of 6 feet, from 605 to 620; it appears, therefore, to be a little nearer the red than the band given by water alone.

The colourless liquid in which we first recognised an absorption-band was ordinary alcohol, and we have since examined three other alcohols of this series, namely, methylic, propylic, and amylic alcohols. They all give a similar band; with each alcohol this band has a different position. The higher the alcohol in the series, the nearer is the band to the red end of the spectrum. Figs. 2, 3, 4 and 5 show these bands.

The saline ethers also give very interesting results; for in all the cases we have examined, we have found a band very similar to the alcohol one, but it is always slightly nearer the blue end of the spectrum. In the case of ethyl iodide another band is visible; this extends from 716 to 724. Probably this band is present in all the compound ethers, but in other cases it is hidden by general absorption. The spectrum given by the iodide is shown in Fig. 9.

In the amylic series we have experimented with the nitrate, acetate, and iodide. All these behave in exactly the same way as the compound ethylic ethers, viz., they all give bands similar to the alcohol band (Fig. 5), but slightly nearer the blue. With amylic iodide (Fig. 6) no second band is visible. It is also of considerable interest to note that amylene gives a band coincident with the one given by the compound amylic ethers. The same band running through each alcoholic series, shows that the band-producing body is unaffected by the acid radical.

Chloroform (Fig. 30) gives a faint absorption extending from 607 to 616, ending on one side very sharply. No band corresponding with the one in methyl alcohol is visible, there is, however, a very dark and sharp band extending from 711 to 717; judging from what occurs in the ethyl series probably this band runs through the whole of the methyl series.

Ether (Fig. 8) gives a spectrum which is remarkably clear and sharp; the most refrangible band coincides in position with the ethyl band (Fig. 3), but it is much darker and somewhat narrower—contracted a little on the less refrangible side, and the termination of the absorption on both sides is very sharp. The second band in ether is similar in position to the less refrangible band in ethyl iodide, but it is wider and darker.

Figs. 10 and 11 represent the absorption taking place with aldehyde and acetic acid; in both cases the absorption is but feeble, and it is only in lengths of 8 feet that we have been able to see these bands.

The next class of bodies examined were those belonging to the benzene series, and we found they gave very clear and interesting absorption-bands. Fig. 12 shows the absorption produced by 8 feet of pure benzene; both bands, the one from 606 to 616, and the other from 703 to 714, are remarkably sharp and dark; there is also a slight absorption extending as far as 678, and ending there so sharply that probably there is a line at that point, and further there is a still fainter shade extending up to 630, also ending sharply. The following drawing (Fig. 13) gives the visible absorption spectrum in 8 feet of the next member of this series, viz., methyl-benzene or toluene. There is much interest in the change which has taken place, the 606 to 616 band has become decidedly fainter, while the 703 to 714 band is as dark as before. Another band, or at all events an absorption ending very sharply at 725, is visible, and the absorption round the 703 benzene-band seems to have cleared away, but the faint absorption about 630 has intensified, and ends sharply at 631.

Fig. 14 gives the absorption produced by the next higher member of this series, xylene. The replacing of the second atom of hydrogen by methyl has carried on the same kind of change as that produced by the first substitution, for the 606 band is now fainter than it was in the toluene, and the 631 shade has developed to a complete band. The two dark bands in the red are as clear as ever. Another feature in the spectra of these compounds is the approach of the bands to the red; with the 703 band this is very marked and very regular. It would certainly seem that as the molecular weight of the compound is increased by the substitution of methyl for hydrogen, so does this band approach the red end of the spectrum.

In this connection we thought it would be of some interest to study still further the effect of substitution upon benzene. We therefore prepared the pure mono- and di-chlorbenzene; the latter was used dissolved in ether. Figs. 16 and 17 show the spectra given by these bodies. The two bands correspond exactly in position with those given by benzene, but the 606 band has become much fainter, exactly the same kind of change which occurred in the case of toluene and

xylene. The chlorine does not affect either the position or character of the less refrangible band.

In connection with these bodies it was of importance to examine naphthalene. A perfectly colourless sample of this body was fused in a 2-feet tube, closed at each end with a transparent glass plug, and having a tube fused into it to allow for the expansion of the contained liquid. The fused naphthalene gave a spectrum shown in Fig 31. There are three bands, and these correspond exactly in position with the two benzene-bands, and with the termination of the faint intermediate absorption. Further, the relative power of all these bodies to produce absorption is a matter of much interest and importance; for instance, a column of 2 feet of naphthalene produces about the same amount of absorption as a benzene column six or eight times as long, and benzene is a far more powerful absorbent than either toluene or xylene. In 2 feet of benzene the two dominant bands and the absorption from the red are distinctly visible. With the same length of toluene the most refrangible, the 606 band, has become decidedly fainter, and the least refrangible is less distinct than the corresponding benzene-band, and with the same length of xylene the only thing which is visible is a very faint indication of the least refrangible band, the other two bands have entirely disappeared.

Phenol gives two bands shown in Fig. 15; the most refrangible of the two agrees in position with the water-band, but it is smaller, and its sharp edge and dark side is on the less refrangible side, the reverse of what occurs with the water band. The least refrangible band is from 679 to 710, therefore a little nearer to the blue than the benzene-band.

In our former communication we described the several visible bands produced by a solution of ammonia, and the experiments we made to convince ourselves that all these bands did belong to ammonia. Fig. 18 shows the bands seen in a 6-feet column of a saturated aqueous solution. The band from 649 to 654 is the darkest; the position of the two more refrangible ones coincide very nearly, the one with the alcohol, and the other with the water-band, but differ in size and character; there is also a still more refrangible band, narrow and sharp, from 566 to 570. Clouded by the general absorption in the red, there is also an indication of a fifth band extending from 698 to 708. The next figure shows the spectrum given by ether saturated with ammonia. If alcohol in place of ether be the solvent a similar set of absorption-bands is obtained. On comparing the two spectra, Figs. 18 and 19, it will be evident that the most refrangible band is absent even in an 8-feet column, possibly in consequence of the mere absence of a sufficient amount of ammonia, the alcohol not taking up as much as the water. The band coincident with the water-band has become fainter in consequence, very probably not of the

absence of water, but of the absence of ammonia, the band coincident with the alcohol-band has become darker, and lastly the band in the red has become far more visible.

It was evidently of much interest to follow spectroscopically the changes which would ensue on replacing the hydrogen in ammonia by methyl, ethyl, &c.

Figs. 20 and 21 give the absorption produced by methylamine, the first by a column of 6 and the next by a column of 4 feet of a 33 per cent. aqueous solution of this body. Here clearly in Fig. 21 is a disappearance of the most refrangible band owing to shortening the length of the column.

On comparing this spectrum with that of ammonia (Fig. 18) it will be seen that the change which has taken place is a fading out of the more refrangible bands and a strengthening of the 649 band. In the shorter length the band in the red is quite visible.

Ethylamine also (Fig. 22) gives a spectrum very like that of ammonia. The dominant ammonia-band has become broader and darker, and a very clear and dark band is seen in the red. Both these bands, as compared with the corresponding ammonia-bands, are nearer the red end of the spectrum. We examined an aqueous solution containing 33 per cent. of ethylamine, and also the pure substance, and we found that they gave similar spectra. The next two (Figs. 23 and 24) give respectively the absorption produced by the di- and tri-ethylamine.

We would point out one or two curious facts which these experiments indicate. When ethyl or methyl is substituted for hydrogen in ammonia, the first thing which seems to occur is that the 649 band becomes broader, and is moved a little towards the red, also that the most refrangible ammonia-band disappears. When the second atom of hydrogen is replaced by ethyl, the 604 band disappears, the 649 band becomes much fainter, the 628 band becomes broader and darker, and finally when all the hydrogen in ammonia is replaced, the 649 band has entirely disappeared, and the 628 band has become very dark and sharp. Further, after each substitution it seems that the least refrangible bands are moved to the greatest extent towards the red end of the spectrum. Again, as far as the visible spectrum goes, ammonia gives the most complicated spectrum, triethylamine the least so, and it is important to note the similarity between the ethylic alcohol-band and those given by di- and tri-ethylamine.

Aniline, as shown in Fig. 25, gives bands similar to those given by ammonia. So similar are they in position that it might be difficult to distinguish these bodies by their visible absorption spectrum; the 649 band in aniline, however, is not so intense as the corresponding

ammonia-band. At the same time the least refrangible band appears always to be more conspicuous in aniline than it is in ammonia, and the next more refrangible band does not coincide exactly in position with the corresponding ammonia-band, but is a little nearer the blue its position being from 646 to 653.

On comparing the aniline spectrum with that of toluidine, it will be seen that as far as it goes there is a close resemblance; we have here another instance of the thickening of the dominant aniline-band. Unfortunately a little but a very persistent colour gave absorption in the green and blue, which rendered it impossible to see whether the two most refrangible bands which are in ammonia and in aniline, are also in toluidine. Judging from analogy we feel confident that they must be there, but that the absorption completely hides them.

The di-methyl-aniline, for which we have to thank Mr. Friswell, gives an interesting spectrum, which, like that of triethylamine, contains but two bands; both these bands correspond to aniline-bands, and therefore to ammonia-bands.

The simplification of the visible spectrum by the complication of the molecule, and the different relationships which exist between bodies formed on the same type, is shown in the last three figures, which give the bands produced by ammonia, dimethyl-aniline, and triethylamine. In the first case none of the hydrogen is replaced, in the other two all of it is.

Fig. 28 gives the spectrum of turpentine. Its most marked characteristic is the existence of two bands, one from 636 to 641, the other from 624 to 628; these bands are united by a considerable amount of absorption. There is also a faint band from 600 to 610, which is coincident with the water-band.

We have been able to find but few liquids which in columns of 6 or 8 feet do not give absorption spectra; in carbon tetrachloride and carbon disulphide we appear to have bodies which do not in these lengths give visible absorption-bands.

XXX.—*On Diquinolyline.*

By Francis R. Japp, M.A., Ph.D., Demonstrator in the Chemical Research Laboratory, Science Schools, South Kensington, and C. Colborne Graham, A.I.C.

The action of the chlorides of the acid radicles upon quinoline has not been studied. With the exception of an observation due to Greville Williams (*Edin. Phil. Trans.*, **21** [3], 394), that acetyl chloride acts violently on quinoline, forming a crystalline, very deliquescent mass, we have been unable to find in the literature of quinoline anything relating to this subject. We therefore resolved to study the action of benzoyl chloride on quinoline at various temperatures.

The quinoline employed was prepared by the method of Skraup (*Sitzungsber. d. Wien. Acad., math. nat. Classe*, 1880, 69), from a mixture of aniline, nitrobenzene, glycerol, and sulphuric acid. The product boiled constantly at 229°.

Equal volumes of quinoline and benzoyl chloride were heated together in a sealed tube. A few crystals separated out on mixing the two substances, but no decided action took place till the temperature was raised to 230°. After heating for some hours to this temperature, the contents of the tube partially solidified on cooling to a crystalline mass. It was found, however, that a slightly higher temperature was more favourable to the progress of the reaction. The contents of a second tube, heated for six hours to 240—250°, solidified completely. The temperature must, however, be carefully regulated, inasmuch as somewhat above 250° a pitchy mass is obtained from which nothing definite can be isolated. The crystalline product from several such tubes was boiled with hydrochloric acid. A somewhat strong acid must be employed for this purpose, as the salts of the new base are decomposed by excess of water into free acid and insoluble base. Moreover, as the hydrochloride is not very soluble in the cold, a considerable volume of acid is required. The hydrochloric solution was filtered from the undissolved resinous mass, extracted with ether to remove benzoic acid together with insoluble resinous matters, and evaporated to a small bulk. On adding caustic soda a crystalline base was precipitated, mixed, however, with unaltered quinoline and dark coloured. Two crystallisations from boiling alcohol yielded a perfectly colourless product in the form of large satiny laminæ, fusing constantly at 191°. On another occasion, however, when a somewhat higher temperature had been employed, the crystals obstinately retained a trace of a pale brown colouring matter, which could not be

removed by crystallisation alone. The presence of this colouring matter did not seem to influence the fusing point or the analytical results. The substance sublimes in colourless laminæ. It is insoluble in water; readily soluble in chloroform and in boiling benzene, crystallising from its solution in the latter solvent on cooling; moderately soluble in hot, almost insoluble in cold alcohol; slightly soluble in ether.

Analysis yielded the following results:—

	Substance.	Carbonic anhydride.	Water.
I	0·2051	0·6332	0·0888
II	0·1975	0·6112	0·0861

III. 0·0820 gram burnt *in vacuo* with copper oxide gave 7·99 c.c. (calibrated vol.) nitrogen at 16·2°, and 714·9 mm. pressure, corresponding to 0·00891 gram nitrogen.

These numbers lead to the empirical formula C_9H_6N:—

	Calculated for C_9H_6N.		Found.			
			I.	II.	III.	Mean.
C_9.....	108	84·38	84·20	84·40	—	84·30
H_6	6	4·68	4·81	4·84	—	4·83
N.....	14	10·94	—	—	10·87	10·87
	128	100·00				100·00

Quinoline, C_9H_7N, on the other hand, requires C 83·71, H 5·43, and N 10·86 per cent. Doubling the above empirical formula, in order to satisfy the law of even numbers, we arrive at the formula of a *diquinolyline*, $C_{18}H_{12}N_2$.

We are unable to offer a satisfactory explanation of the reaction in which this diquinolyline is formed. The reaction is not of a simple character, large quantities of resinous matter being produced at the same time. As yet we have been unable to prepare the compound in any other way, but the experiments in this direction are not yet concluded.

The substance is a weak base, the salts of which are stable in presence of an excess of strong acid, but are decomposed by water. The addition of an excess of water precipitates the base so thoroughly from the solutions of its salts, that ammonia produces in the filtered liquid only a slight opalescence. The salts with colourless acids are of a pale yellow, even when prepared from perfectly colourless base. All the salts which we have examined are diacid.

Platinochloride.—This salt cannot be prepared by adding an aqueous solution of platinic chloride to a solution of the base in hydrochloric acid, since in this way a mixture of platinochloride and free base is precipitated. It was, however, obtained by the following method: A quantity of the base was dissolved in sufficient concentrated hydrochloric acid to keep it in solution in the cold, and the liquid was poured into an excess of a solution of platinic chloride in concentrated hydrochloric acid. The platinochloride separated out almost immediately as a bright yellow granular precipitate, which under the microscope was seen to consist of fern-shaped aggregations. The precipitate was filtered off, washed with concentrated hydrochloric acid, and dried in a desiccator over soda-lime. The salt thus dried did not lose weight on heating for some hours to 80°. A platinum determination gave the following result:—

0·3448 gram yielded on ignition 0·1013 gram platinum.

	Calculated for $C_{18}H_{12}N_2.2HCl.PtCl_4$.	Found.
Pt in 100 parts.....	29·53	29·38

Various unsuccessful attempts were made to prepare a monacid platinochloride. By boiling the diacid salt repeatedly with alcohol as long as the liquid acquired a yellowish tinge from dissolved platinic chloride, a substance was obtained, which gave a percentage of platinum approximating to that demanded by the monacid salt; but a subsequent examination of this substance showed it to be a mixture, inasmuch as cold chloroform extracted from it a quantity of free base.

A portion of the base was heated with methyl iodide in a sealed tube, but no combination took place, even at a temperature of 150°.

The study of diquinolyline will be continued.

ANNIVERSARY MEETING.

March 30th, 1881.

Dr. Roscoe, F.R.S., President, in the Chair.

The following Report was read by the President:—

On behalf of your Council, I have the honour to report as follows on the present condition of the Society.

A comparison of the scientific and other work accomplished by the Chemical Society during the past twelve months with that of former years, justifies the statement that at no period of its history has it been so flourishing as at the present time. The number of Fellows is larger than it has ever been, being 1,096 as against 1,034 at the last anniversary. The communications made to the Society by Fellows and others have also increased both in importance and in number, whilst the interest displayed by the attendance of Fellows at the Society's meetings has certainly not diminished. Then the finances, an important item in the success of a society like yours, are in a satisfactory condition, the Treasurer's report showing an income of £2,916 as against £2,719 for the preceding year.

The various important departments of the Society have worked satisfactorily during the past session. Since March 30th, 1880, no fewer than 113 papers have been read before the Society as against 75 read in the preceding year. The primary object of the Society is the general advancement of Chemical Science, accomplished by the reading and discussion of original communications, and so long as the quality and number of such communications is sufficient to occupy the time of the meetings, the delivery of lectures, except on special occasions, may be properly dispensed with. Fortunately this has been the case during the past year, and hence no lectures have been delivered.

A glance over the publications contained in the Transactions of the Society for the session 1880–81 suffices to bear out the statement that English chemists are now well to the fore amongst those of other nations in advancing their common science.

The other scarcely less important portion of your Journal, the

Abstracts, continues to uphold its character for accuracy and usefulness, and the appreciation and support accorded to this feature of the Society reminds us of the thanks the Society owes to the originator of this system, Dr. Williamson.

Considerable additions have been made to the Library of the Society since the last anniversary, and the books have been rearranged, being now classified according to subjects, and the shelves labelled accordingly.

Two Card-catalogues have been prepared, the one arranged according to authors' names, the other according to subjects.

The Research Fund, founded in 1876 by the donation of £1,000 by Dr. Longstaff, now amounts to £4,427. Many of the City Companies have aided the foundation of this fund. The Goldsmiths' Company gave the handsome sum of £1,000, whilst the Clothworkers', the Mercers', the Grocers', the Merchant Taylors', and the Skinners' Companies have all contributed donations. To the Drapers especially (next to the Goldsmiths) the Society is much indebted, as they have been donors of £100 for several years, and are continuing their subscription. The Fund is also indebted to several of our Fellows for substantial aid. Dr. De La Rue has on three occasions presented the fund with £100, Dr. Gladstone has twice given a like sum, whilst Dr. Frankland and Mr. P. H. Worsley each make an annual donation of £10. Up to the present time 37 grants have been made in sums varying from £100 to £5, and amounting in all to £1,021.

Although any attempt to review the progress which our science has made during the past twelve months would here be out of place, I may perhaps be allowed to take up the thread dropped by your late President and say a word or two on a few of the more important discoveries of the year.

In the first place, then, the statement that the halogens have actually been dissociated has not proved to be correct, in so far as that any two or more bodies differing from the original one in properties have been obtained. The observed alteration in the density of chlorine has been admitted by Victor Meyer to be due to some unexplained error, whilst in the case of iodine the fact, now well established, of its diminution in density at a white heat is unaccompanied by any proof of the actual decomposition of the element, and can be explained by dissociation of the molecule.

The solar and stellar evidence concerning the question of the decomposition of the metals is still being accumulated by Mr. Lockyer, but as yet it has not assumed a sufficiently cogent form to enforce acceptance of the fact from chemists in general, perhaps, as it has been well said, because the nature of the proof is not one with which they are familiar.

The researches of Captain Abney, referred to in the last Annual Report, have since that time, and in conjunction with Lieut.-Colonel Festing, been continued with conspicuous success, and have given birth to a discovery of the highest interest and of the greatest possible promise. This is no less than a distinct physical test of the existence in organic compounds of the organic radicals, and a means of recognising the chemical structure of an organic compound by means of the spectroscope. This result, which naturally opens out an entirely new field for investigation, and effects for the organic metals that which ordinary high temperature spectrum analysis does for the inorganic metals, is accomplished by photographing the absorption spectra of organic compounds in the infra-red part of the spectrum. In these invisible portions, characteristic and distinct absorption-lines and bands occur for each organic radical. The ethyl compounds all show one special "ethyl" band, the methyl compounds a special "methyl" band; and thus, just as a glance at the luminous portion of the spectrum satisfies us of the presence of calcium, and lithium, and rubidium, so a simple inspection of these infra-red photographs enables us to ascertain the presence of the various organic radicals. This investigation is still in its infancy, but one of greater importance to chemists has seldom, if ever, been communicated to the Society.

I may perhaps be here allowed to add that an equally important confirmation of certain fundamental views of modern chemistry has been obtained from a discussion of electric phenomena by Helmholtz, an account of which is to be given to us in his forthcoming Faraday Lecture.

Ladenburg's researches on the alkaloïds have met with further success, as he has, since our last anniversary, effected the synthesis of atropic acid, and has from this obtained tropic acid, one of the constituents of atropine.

The anticipation of Dr. De La Rue in the last Anniversary Address that the experiments of Baeyer must ere long result in the discovery of a method for the artificial production of indigo has been confirmed in a remarkable manner; for not only has this most important discovery been actually made, but the manufacture of artificial indigo is now being undertaken by competent hands. The point of departure of Baeyer's epoch-making discovery is cinnamic acid; the last link in the chain is orthonitrophenylpropiolic acid, from an alkaline solution of which pure indigo-blue separates out on heating with grape-sugar. The yield of indigo is about 40 per cent. of the propiolic acid, the theoretic amount being 68 per cent. On the question of the constitution of indigo Baeyer reserves judgment, though he believes that the molecule contains at least twice $C_{16}H_{10}N_2O_2$.

A theoretical question of great interest has lately been the subject

of much verbal as well as experimental discussion. A favourite idea of Kolbe's, that the four combining units of each carbon-atom are not of equal value, appeared to receive experimental verification from Schreiner's researches on the methylethylcarbonic ethers. If the carbon-atom is unsymmetrical, two isomeric ethers of the above composition must exist. Schreiner obtained one body of this composition by heating sodium methylate with chlorocarbonic ethyl-ether, and this had a boiling point of 104°; he then acted upon sodium ethylate with chlorocarbonic methyl-ether, and found that the product boiled at 115·5°, and had a lower vapour-density than the compound obtained by the first process.

Geuther and Roese have examined the same question, and their results flatly contradict the statements of Schreiner. They, or rather the latter chemist, prepared all the carbonic ethers from methyl to amyl, as well as many of their derivatives, and having carefully compared their properties, came to the conclusion not only that those which contain the same alcohol-radicals are identical in every particular, but that they yield identical products. Thus the ethylmethyl-ether obtained from chlorocarbonic ethyl-ether and methyl alcohol is absolutely identical with methylethyl-ether prepared from chlorocarbonic methyl ether and ethyl alcohol, the explanation of the differences observed by Schreiner being the difficulty of obtaining the products in the pure state.

Concerning the new Earth-metals, I may mention in the first place Marignac's examination of samarskite, in the course of which he has recognised two new metals, one yielding colourless salts, like yttria, but having a much higher atomic weight than the latter, and, like terbia, forming only a slightly soluble double potassium sulphate. This he christens yttrium α. Another, yielding yellow salts, and exhibiting an identical spectrum with Delafontaine's decipium, but differing from this in its atomic weight, Marignac terms yttrium β. Whether these last-named are identical, or are mixtures of two or more elements, must be left for future investigation. Then Nilson, by very careful experiments, made on large quantities of material, has prepared scandia and ytterbia in a state of great purity, and has accurately determined their atomic weights, as also the properties of many of their salts. The spark-spectra of these metals have been mapped by Thalén. In addition to this, Clève has obtained thulium and the true erbia in a state approaching to purity, and Thalén has proved that the earth thulia, like erbia, possesses the property of giving an emission spectrum when heated to whiteness. Some of these metals yield no absorption-bands in the visible spectrum, but they may very possibly exhibit distinctive lines in the infra-red when examined by Abney's method.

Since the last Anniversary the Society has lost two foreign Members and ten Fellows, viz.:—Prof. Heintz, of Halle; Prof. Mulder, of Amsterdam. Sir B. C. Brodie, Dr. Stenhouse, Prof. Wm. Hallowes Miller, Mr. James Tennant, Mr. W. W. Stoddart, Rev. D. W. Ladley, Mr. William Arnot, Mr. A. C. Bruce, Mr. Thomas Eltoft, Mr. Richard Johnson.

William Heinrich Heintz, Professor of Chemistry at the University of Halle, was elected a Foreign Fellow of the Chemical Society on February 18th, 1876. His name will be generally remembered by his researches on the fats, and by the synthetic production of margaric acid. Amongst his other very numerous contributions to our science (no fewer than 167 original communications being mentioned in the Royal Society list under the name of Heintz), I may remind you of his study of the action of monochloracetic acid on alcoholates and phenates, giving rise to a long list of interesting bodies, for example, that of the action of this acid on ammonia, which gives rise to the di- and tri-amido acids, such as ethylglycollic and phenylglycollic acids. Heintz investigated their constitution, and explained why bodies of this class act at the same time as monobasic acids and ethers. His recent and unfinished investigations on the acetone bases obtained by saturating a mixture of acetone and ether with ammonia, the last of which was published in June, 1880, will be in the memory of many Fellows.

Gerardus Johannes Mulder, Professor of Chemistry at the University of Utrecht, was elected a Foreign Member of the Society on May 1, 1860. The name of Mulder is associated with a remarkable controversy, now almost forgotten, viz., that concerning the existence of the hypothetical organic radical common to all the proteïds. This was believed by him to be free from sulphur, and to it he gave a formula containing 40 atoms of carbon and 31 of nitrogen, supposing it to combine with sulphur and phosphorus in the proportion of 20 atoms of the oxide to 1 atom of phosphorus sulphide, to form fibrin, albumin, caseïn, &c.

Liebig then showed that the substance described by Mulder as proteïn dioxide, really contains sulphur, and proved that no proteïd body can be obtained free from this element. Upon this Mulder attempted to remodel his proteïn theory, but unsuccessfully, and now, as Gmelin remarks, nothing remains of this theory but the name. Still the researches of Mulder on this subject have proved of great value, as breaking ground in a new and most difficult field, and thus preparing the way for the subsequent investigations of Liebig, Kühne, Hoppe-Seyler, and others.

Of more lasting importance were Mulder's researches on wine, his

treatise on the "Chemistry of Wine," translated into English by the late Dr. Bence Jones, being still a standard work.

Of the losses amongst our Fellows, the most severe which the Society has sustained is that of Benjamin Collins Brodie, who, so long ago as the year 1845, became connected with this Society as a Fellow; from the years 1850 to 1854 served as one of our Secretaries, and in the year 1860 occupied the position of President of our Society. Son of the great surgeon of the same name, Brodie was early imbued with the liberal and high-minded views of his father, and determined to devote his life and energies to the prosecution of pure science. He was born in London in 1817, and educated first at Harrow, under Longley, and afterwards at Balliol, where he took his Master's degree in 1842. Unable at Oxford to obtain that knowledge of the methods of original research so absolutely essential to the young scientific chemist, Brodie naturally betook himself to Giessen, where Liebig's name drew students from every land. At once commencing original investigation, Brodie, at Liebig's suggestion, carried out analyses of certain waxes obtained by Gundlach, on feeding bees with different kinds of sugar. The results thus obtained led him, on his return to England, to continue his examination of beeswax, and from his private laboratory in the Albert-road, his celebrated researches on the chemical nature of wax were published. These are found in the *Phil. Trans.* for 1848, pp. 147—170, and 1849, pp. 91—108, and for them he received in 1850 the Royal Medal of the Royal Society. These researches will always remain remarkable, not only as having given a successful solution of a difficult problem, but also as having proved by careful and exact work, the existence in wax of solid alcohols. The unexpected discovery of these bodies completely confirms the truth of the views concerning the existence of a homologous series of alcohols, first enunciated by Schiel and Gerhardt, and thus places in a firm position one of the chief pillars of the organic portion of our science.

Brodie's next research was not inferior to his first either in importance or in workmanship. In 1850 he published his memoir "On the Condition of Certain Elements at the Moment of Chemical Change" (*Phil. Trans.*, 1850, pp. 750—804; *Chem. Soc. J.*, **4**, 194), in which he carefully investigates the remarkable reducing action exerted by peroxide of hydrogen. This anomalous action was satisfactorily explained by Brodie, who pointed out, not only that the second atom of oxygen in this and similar peroxides is retained in a loose state of combination, but that when it is brought into contact with silver oxide, a true synthesis of oxygen occurs, two atoms of this element uniting to form one molecule of free oxygen. These results led him

to consider the constitution of the alcohol-radicals (*Chem. Soc. J.*, **3**, 405), and to assert in 1851 the important fact, now universally admitted, that the molecule of ethyl in the free state contains four atoms of carbon. To him also we owe the prediction of the possible existence of the so-called "mixed radicals," now known as "paraffins," a prediction soon afterwards experimentally verified by Wurtz.

In 1853 he published his interesting observations on the conversion of yellow phosphorus into the red modification by heating it to 200° in presence of a mere trace of iodine (*Chem. Soc. J.*, **5**, 289). Another very important and difficult investigation, which occupied much of his attention about this time, was the question of the purification of graphite (*Ann. Chim. Phys.* [3], **45**, 351) and the determination of its atomic weight (*Phil. Trans.*, 1859, 249; *Chem. Soc. J.*, **12**, 261). By heating graphite with strong nitric acid and chlorate of potash, Brodie showed that, unlike all the other modifications of carbon, it yields a crystalline graphitic acid. The existence of this interesting body led Brodie to the conclusion that graphite may be considered as a peculiar radical, to which he gave the name of graphon. Nor was this research wholly of theoretical interest, for the process proposed by Brodie for the purification of graphite has been applied on the large scale, and proved itself of commercial value.

In the year 1855, Brodie was appointed to the Waynflete Professorship of Chemistry in the University of Oxford, a position which enabled him to throw all his influence into forcing the recognition of chemical science as a proper object of academic training. Under his fostering care, the science which had hitherto been so long neglected, gave signs of life, and new laboratories and lecture-rooms were built, to which students flocked in numbers. The discovery of those singular and dangerous bodies, the peroxides of the organic radicals (*Phil. Trans.*, 1863, 407; *Chem. Soc. J.*, **17**, 264), was made in the laboratory of the new museum of Oxford. The same laboratory afterwards saw the minute and careful investigation of ozone (*Phil. Trans.*, 1872, 432; *Proc. Roy. Soc.*, **20**, 472), which proved beyond doubt that Odling's suggestion that the molecule of ozone is represented by the formula O_3 is both necessary and sufficient to explain all the observed phenomena.

Next, we find him experimenting on the synthetic production of the hydrocarbon methane, as well as of formic acid, by the direct union of hydrogen and carbon monoxide under the influence of the electric spark. Then he examined the effect of an induced electric current upon pure and dry carbon dioxide, and proved that this gas is partially decomposed, with formation of carbon monoxide and oxygen, the latter gas being converted into ozone.

This was Brodie's last experimental investigation. Ere long he

resigned the Chair of Chemistry at Oxford, regretted by the whole University, and retired to his charming seat on the summit of Box Hill. Neither his own scientific activity nor his deep interest in the scientific work of others ceased on his withdrawal from professional life. Before his retirement, he had put forward in the "Calculus of Chemical Operations" (*Phil. Trans.*, 1866, 781, 860; *Chem. Soc. J.*, **21**, 367), views altogether novel respecting the nature of chemical change. In place of the usual mode of considering this as due to a change in the relative positions of the atoms of which matter is composed, Brodie founds his theory of the constitution of chemical elements and compounds on the simple volume-relations, discovered by Gay-Lussac, to exist between these substances in the gaseous state. To hydrogen Brodie gives a simple symbol, because the unit of hydrogen can, as he expresses it, be conceived as made at once by one operation, whilst to oxygen he gives a double symbol, because it cannot, according to him, be made by less than two operations. The element chlorine is supposed to be made up of three operations, and a triple symbol is given to this body. Concerning the probable or possible decomposition of the elements, Brodie naturally speculates. His analysis had led him to suspect that "chemical substances are really composed of a primitive system of elemental bodies analogous in their general nature to our present elements, some of which we possess, but of which we possess only a few" (*Ideal Chemistry*, p. 54). But no experimental evidence of this fact was offered by him, and none of a satisfactory character was otherwise forthcoming, until Victor Meyer announced his belief that chlorine was capable of undergoing decomposition at high temperatures. As I have already stated, further experiment has thrown doubt upon these first conclusions of Victor Meyer.

Whatever may be the verdict of the future as to the value of Brodie's "Calculus," there is no doubt that science is indebted to him for an altogether new view of chemical combination obtained by a systematic analytical process.

Although he had been absent from our meetings for some years, and was therefore not personally known to many of the younger Fellows, all those who have attended in the rooms in Cavendish Square and old Burlington House, will remember the active interest which Sir Benjamin Brodie took in the affairs of the Society, his lively, energetic, and earnest manner, and his perfect courtesy. Those who were fortunate enough to secure his friendship valued it as that of a true, generous, and noble-hearted man.

The following is a list of Brodie's papers published in the Society's Journal:—

1. "On the Alcohol-radicals, and on the Formation of Ethyl," **3**, 405.
2. "On the Condition of certain Elements at the moment of Chemical Change," **4**, 194.
3. "On the Action of Iodine on Phosphorus," **5**, 289.
4. "Further Experiments as to the Reduction of Metallic Oxides by Peroxide of Barium," **6**, 304.
5. "On the Combination of Carbonic Oxide with Potassium," **12**, 269.
6. "On the Atomic Weight of Graphite," **12**, 261.
7. "On Oxidation and Deoxidation Produced by the Alkaline Peroxides," **16**, 316.
8. "On the Peroxides of the Radicals of the Organic Acids," **17**, 264.
9. "On the Organic Peroxides Theoretically Considered," **17**, 281.
10. "Calculus of Chemical Operations." (Part I), **21**, 367.

JOHN STENHOUSE was the eldest son of William Stenhouse, of the firm of John Stenhouse and Co., calico-printers, Barhead, Glasgow, by his wife Elizabeth Currie. He was born at Glasgow on the 21st October, 1809, and was the only one of their children who outlived infancy. He was educated first at Glasgow Grammar School, and subsequently at Glasgow University, where he studied from 1824 to 1828.

The weak eyesight and delicate constitution he inherited from his father, and which in after life was the cause of so much suffering to him, prevented him from following literature as a pursuit, although his tastes in early life inclined in that direction. He consequently turned his attention to science, and devoted himself to chemistry, which he studied under Professor Graham and Dr. Thomas Thomson, his training being first acquired at the Andersonian University, Glasgow: it was probably on this account that he always took so deep an interest in this Institution. During his lifetime he used all his interest to obtain bursaries, and otherwise promote the study of his favourite science, and by his will he left a legacy to found a scholarship in connection with the Chemical Chairs of the College.

In 1837, 1838, and 1839, he attended the chemical lectures at the University, and shortly afterwards left Glasgow for Giessen, where he continued his studies under Liebig, and made the acquaintance of many of his fellow-pupils, whose names have since become illustrious as workers in the field of chemical research. He was with Liebig at Giessen about two years, and then returned to Glasgow, where he remained until the failure of the Glasgow Commercial Exchange deprived him of the fortune bequeathed him by his father, which had hitherto rendered him independent.

Stenhouse received his degree of LL.D. from the University of Aberdeen in May, 1850, and it was about this time that he was an unsuccessful candidate for the Professorship of Chemistry at Owens College. He left Glasgow for London in January, 1851, and in the following month was appointed Lecturer on Chemistry to the Medical School at St. Bartholomew's Hospital, but was obliged to resign the appointment in 1857 owing to a severe attack of paralysis, which, although it deprived him of the use of his limbs to a great extent, did not seem to affect his intellectual powers to any appreciable degree. He then went to Italy, where he resided with his mother until her death, which took place at Nice in February, 1860. He returned to England in June of the same year, fitted up a laboratory, and again commenced scientific investigation with that wonderful energy which was so characteristic of him, and which enabled him to continue his work in spite of the obstacles occasioned by his bodily infirmities. In 1865 he succeeded Dr. Hofmann as one of the non-resident Assayers to the Royal Mint, but was deprived of the appointment when the office was abolished by Mr. Robert Lowe in 1870. In November, 1871, a Royal Medal of the Royal Society was awarded to him for his long-continued chemical researches, many of which have proved of great value in the arts and manufactures.

During the last four years of his life the weak eyesight to which he had been a martyr during his residence in Italy, returned under a different form: he was seized with an attack of rheumatism in the eyelids, which became chronic, compelling him to live almost constantly in a darkened room, and at times causing him intense pain. His health during this time varied very much, but it was not until within a few weeks of his death that he became sensibly feebler; he ultimately sank into a sleep, and died a painless death from decay of nature in the early morning of the 31st December, 1880. On the 6th of January he was buried in his father's grave in the High Church new cemetery in Glasgow, on the north side of the Cathedral.

Dr. Stenhouse was a Fellow of the Royal Society, and one of the few surviving founders of the Chemical Society; a Fellow of the Institute of Chemistry, an Honorary Member of the Berlin Chemical Society, as also of the Philosophical Society of Manchester, and the Pharmaceutical Society of Great Britain.

During the past 40 years Dr. Stenhouse published more than 100 papers on the results of his numerous investigations, which appeared in the Transactions and Proceedings of the Royal Society, the Memoirs and Journal of the Chemical Society, the Philosophical Magazine, Liebig's Annalen, and elsewhere, a list of which down to 1873 will be found in the Royal Society's Catalogue of Scientific Papers. An inspection of the titles of these papers shows how large

a part of his work relates to what may truly be called "organic chemistry," the chemistry of compounds found in organised bodies, and especially in plants. His first paper, published in 1839 in the *Annalen der Chemie und Pharmacie*, **31**, 148, and entitled "Darstellung und Analyse des Hippursauren Æthers," related to a compound from the animal kingdom, but this is an exception, and we find four or five papers on tannin and its products of decomposition, others on the essential oils of elemi, olibanum, laurel, hyssop, assafœtida, cinnamon, leafte; on alkaloïds such as theine, sparteine, scoparine, berberine, and wrightine, besides other carbon compounds, such as mannitol and erythrol, aloïn, meconic and comenic acids, euxanthone, furfuraldehyde and fucusaldehyde, xanthoxylin, chloropicrin, thymol, larixin, &c., and numerous benzene and naphthalene derivatives. The lichens, however, received the largest share of his attention: he has published no fewer than 18 papers on the principles contained in these plants and the derivatives obtained from them, amongst which those on the derivatives of the dihydric phenol, orcinol, are specially noteworthy, including as they do a very complete series of the chloro-, bromo-, iodo-, nitro-, nitroso-, and amido-derivatives of that compound. It is a fact worth mentioning that one of the last communications made by him to our Society was on Betorcinol, a homologue of orcinol he had discovered some 32 years previously. It is but seldom that a chemist lives to complete a work begun so long before.

Although his labours in pursuit of purely scientific knowledge are fully recognised, his contributions to technological science are not so generally known. He was the author of many ingenious and useful inventions in dyeing, waterproofing, sugar manufacture, and tanning; but probably the greatest and most permanent benefit has been conferred by his application of the remarkable absorbent properties of wood-charcoal to disinfecting and deodorising purposes. This took the form of charcoal air-filters and charcoal respirators; the latter are not only of great value in various manufacturing operations in preventing the deleterious effects of noxious and poisonous fumes and vapours, but are most useful to persons suffering from bronchitis or similar affections of the chest.

Of Dr. Stenhouse's personal character those who knew him intimately could never speak too highly; his honesty of purpose and straightforwardness made his friendship doubly valuable, whilst his general conversation and fund of pleasing anecdote rendered him a most pleasant companion. The earnest religious convictions and unaffected piety shown in the ordinary affairs of life were as remarkable as his ingenuity and quick perception in scientific matters. These, combined with his unflagging industry and patience under great bodily

suffering, enabled him to continue his researches with unabated vigour down to the close of his long scientific career.

Professor WILLIAM HALLOWES MILLER was also an original Fellow of the Society, having been elected on February 23, 1841, and his name is inseparably connected with one of the most important of the sciences allied to chemistry, viz., mineralogy, and especially with the crystallographic department of that science. Of the numerous methods of notation proposed by crystallographers, only two have survived the test of experience, and the systems of Miller and of Naumann are the only ones now in use. Of these, the latter is perhaps more generally employed by chemists, as it more readily adapts itself to the requirements of the general student; but in matters of calculation Miller's system is greatly to be preferred, whilst as a method of representing the positions and the mutual relations of a crystal, as well as its cleavage and optical orientation, it stands without a rival. Possessing these and other advantages, it would seem that the final method of considering the morphology of crystals will be that given to us by Professor Miller. As proof of the high estimation in which Miller's nomenclature is held on the Continent, I may mention that in the *Zeitschrift für Mineralogie* the two notations of Miller and Naumann are always written side by side.

As an accurate experimentalist Miller also claims the regard of chemists, for it is to him that we owe a classical example of exact measurement. His paper in the *Phil. Trans.* for 1856, in which he describes in detail "the operations for restoring the value of the old standard of weight, constructing the new standard of a different value; for constructing various derived standards, and for establishing the relative value of the kilogramme," is one which all young chemists who desire to know what experimental accuracy really means would do well to study.

In character simple, gentle, and unobtrusive, Miller possessed a knowledge of physical science in accuracy and extent equalled by few, and leaves a name honoured by all who have the progress of science at heart.

Mr. RICHARD JOHNSON, J.P., of Kemnal Manor, Chislehurst, who died on the 16th of February, 1881, in the 72nd year of his age, was a native of Manchester, where he was the head of the firm of Richard Johnson and Nephew, wire-drawers, Bradford, near Manchester; and of the firm Richard Johnson, Clapham, and Morris, metal merchants. In Manchester he held a highly respected position, and was for many years a member of the Chamber of Commerce, holding at one time the post of President of this body. He showed great interest in educa-

tional matters, and subscribed during his lifetime very largely to the funds for the extension of the Manchester Grammar School, and of the Owens College.

Mr. Johnson was elected a Fellow of the Chemical Society on May 6th, 1858, and, in conjunction with the late Dr. Crace Calvert, published the following chemical investigations:—

"On Alloys," *Brit. Assoc. Report* (1855), Part II, pp. 50—51.

"On the Chemical Changes which Pig-iron undergoes during its Conversion into Wrought-iron," *Phil. Mag.*, **14** (1857), pp. 165—175.

"On the Relative Powers of Metals and Alloys to conduct Heat," *Phil. Trans.*, Part I.

"On the Specific Gravities of Alloys," *Brit. Assoc. Report* (1859), Part II, pp. 66—67.

"Conductibility of Mercury and Amalgams," *Phil. Trans.* (1859), pp. 831—836.

"On the Hardness of Metals and Alloys," *Manchester Lit. and Phil. Soc. Mem.*, **15** (1860), pp. 113—121.

"On the Action of Sulphuric Acid on Lead," *Chem. Soc. J.* (1863), pp. 66—72.

"Action of Sea-water upon Certain Metals and Alloys," *Manchester Lit. and Phil. Soc. Proc.*, **4** (1865); also *Chem. Soc. J.*, **4** (1866), 434—454.

"Recherches sur les alliages de cuivre et d'étain. Observations relatives à une communication précédente de M. Riche," *Compt. rend.* (1869), pp. 192—193.

These investigators, in conjunction with Mr. G. C. Lowe, published an investigation "On the Expansion of Metals and Alloys," *Chem. News*, **3** (1861).

Mr. Thomas Eltoft was elected a Fellow on January 18th, 1872. He was born in Accrington in 1845, and when a young man displayed great aptitude for the study of chemistry, becoming the Teacher of Chemistry in the Mechanics' Institution of his native town. Later on he was appointed Senior Assistant to our Treasurer, Dr. Russell, a post which he held for some years. On his resignation he obtained the Lectureship on Chemistry in the City of London College, Charterhouse Schools, and at some of the guild and other metropolitan schools, and lately at the Bedford College. Mr. Eltoft published several works on Analysis, which have had a considerable sale. As a teacher he was much esteemed by his numerous pupils, and he has left a memory which will not soon be forgotten.

Mr. A. Cameron Bruce, M.A., was elected a Fellow on December

5th, 1872. He afterwards held the post of Professor of Chemistry at Queen's College, Birmingham, and was also a colleague of Dr. George Gore at King Edward's School, where he was appointed as Science Master. He was born at Methlick, in Aberdeenshire, in 1845, and educated at the new Grammar School and the University of Aberdeen. After obtaining his degree, he went to teach in a school at Brighton, and gave a course of lectures on Chemistry to the Brighton Association for the Higher Education of Women. He took an active part in the Birmingham Philosophical Society, but ill-health necessitated his withdrawal from active life in 1879, and he died on March 21st, 1880.

Mr. James Tennant, the well-known mineralogist of the Strand, was elected a Fellow of the Society on March 1st, 1877. His collection of minerals, fossils, and geological specimens was perhaps the largest in the hands of one individual in London. He was the author of several descriptive catalogues of gems and precious stones; another on the jewels belonging to the Crown, preserved in the Tower; and conjointly with Professors Ansted and Mitchell, a treatise on Geology, Mineralogy, and Crystallography, published in "Orr's Circle of the Sciences." Mr. Tennant held for many years the Professorship of Geology and Mineralogy at King's College, London.

Mr. William Walter Stoddart was elected a Fellow of this Society on December 17th, 1868. He showed an early taste for chemistry, and contributed various papers on pharmaceutical subjects, in which he took especial interest. Mr. Stoddart was for two years President of the British Pharmaceutical Conference, and took an active part in the management of the Bristol Pharmaceutical Association; and a series of papers on Bristol pharmacology have appeared in the Pharmaceutical Journal from his pen. For several years Mr. Stoddart held the appointment of Public Analyst for the city and county of Somerset, city of Salisbury, and the boroughs of Bridgewater, Chard, and Devizes.

The Rev. D. W. Ladley was elected a Fellow of the Society on February 18th, 1875. As a member of a religious community Mr. Ladley could devote only a limited portion of his time to the study of Science, to which his natural tastes inclined him.

Mr. William Arnot was a native of Falkirk, where he spent the early years of his life. In his school days he showed a peculiar aptitude for chemistry and the kindred sciences; these he afterwards

studied in Glasgow under the late Dr. Penny and others. His first appointment was that of Gas Manager at Falkirk, and in the following year he went to Liverpool as Chemical Superintendent of a sugar refinery there. On the appointment of Dr. Penny to the Directorate of the North and South Esk River Purification, he removed to Lasswade, near Edinburgh, as his resident assistant; and, on the death of Dr. Penny in the following year, he succeeded him as Director. This position he held till the termination of the agreement between the riparian proprietors and the papermakers. Mr. Arnot then removed to Kirkintilloch to conduct an alkali-work of his own, but not succeeding, he went to Edinburgh in 1877 as Consulting and Analytical Chemist and Chemical Engineer. He was Public Analyst for the counties of Roxburgh and Selkirk, and the burghs of Galashiels, Hawick, Kelso, and Selkirk; and was Examiner in Paper for the City and Guilds of London Institute.

He was the author of several papers on matters relating to manufacturing chemistry, such as "Notes from the Laboratory of a Sugar Refinery," "River Pollution Papers," "The Sphere of Chemistry in the Paper Mill," &c. He was a member of the Society of Arts of London, and in 1877–78 he delivered a series of six Cantor lectures before that Society on "Technology of the Paper Trade," which were much appreciated by papermakers in all parts of the world. He died at Bridge of Allan in the 38th year of his age, from the effects of a severe attack of rheumatic fever.

Mr. Richard Adie was born in Edinburgh in 1810. He commenced business as an optician in Liverpool in 1834, and carried it on till 1875; he also succeeded in 1855 to the business of his father in Edinburgh. He was the author of several papers on physical subjects, published in our own Journal, in the *Philosophical Magazine*, and in the *Edinburgh New Philosophical Journal*. He was elected a Fellow of the Chemical Society in 1856.

The Council have awarded the first Longstaff Medal to Professor Thorpe, of the Yorkshire College, Leeds. When Dr. Longstaff gave to the Society £1,000 for the purpose of founding the Research Fund, he stipulated that a medal of not less value than £20 should be awarded at least once in every three years, and that it should be given to the Fellow of the Society who, in the opinion of the Council, had done the most to promote Chemical Science by Research since the period of the last award. Subsequently it was resolved by the Council, with

Dr. Longstaff's approval, that a bronze medal and purse of £20 be given, the medal to be called the Longstaff Medal.

The Society may, I think, be congratulated, not only upon having this medal to bestow, but upon the way in which the medal has been prepared. For the really artistic and life-like portrait of the donor the Society is indebted to Mr. A. Bruce Joy, the well-known sculptor, to whom, in the name of the Society, I offer our best thanks. The engravers, Messrs. Wyon, have in like manner spared no pains in the execution of their part of the work; and, lastly, the Society is much indebted to the kindness of the Deputy Master of the Royal Mint for striking the medal and taking charge of the dies.

Professor Thorpe: I consider it a special privilege that it falls to my lot to present to you, as one of my oldest and most distinguished pupils, the first Longstaff Medal awarded by the Chemical Society for the best series of original investigations in Chemistry, published in England during the past three years, amongst which I may mention, as the most important, your discovery of phosphorus pentafluoride, that of the occurrence of heptane in *Pinus sabiniana*, giving accurate determinations of its physical constants; and, lastly, the valuable contributions to Physical Chemistry in your researches on the relation between the molecular weight of substances and their specific gravities when in the liquid state. I trust that this recognition by the Chemical Society of your varied and successful labours will stimulate you to further efforts, and that before long the Society may be benefitted by other communications from your laboratory.

Papers read before the Chemical Society from April 1st, 1880, to March 17th, 1881:—

I. "On Betorcinol and Some of its Derivatives:" by J. Stenhouse and C. E. Groves.

II. "Note on Chemical Equilibrium:" by M. M. P. Muir.

III. "Preliminary Note on the Action of the New Diastase, 'Eurotin,' on Starch:" by R. W. Atkinson (Tôkiô).

IV. "Note on the Products of the Combustion of Coal-gas:" by L. T. Wright.

V. "On the Polysulphides of Sodium:" by H. Chapman Jones.

VI. "On the Reflection from Copper, and on the Calorimetric Estimation of Copper, by means of the Reflection Cuprimeter:" by T. Bayley.

VII. "On Pyrene:" by Watson Smith and G. W. Davies.

VIII. "An Analysis of the Ash of the Wood of two Species of Eucalyptus:" by Watson Smith.

IX. "On the Action of Organo-zinc Compounds on Quinones:" by F. R. Japp.

X. "On the Lecture Illustration of Chemical Curves:" by E. J. Mills.

XI. "On the Analysis of Organic Bodies containing Nitrogen (*cont.*):" by W. H. Perkin.

XII. "On the Volatilisation of Solids *in vacuo*:" by W. Douglas Herman.

XIII. "On the Determination of Nitric Acid as Nitric Oxide by Means of its Reaction with Ferrous Chloride:" by R. Warington.

XIV. "On the Six Possible Isomeric Dibromotoluenes, and other of the Bromo- and Nitrobromo-derivatives of Toluene related thereto:" by R. Nevile and A. Winther.

XV. "On the Action of Sodium on Phenyl Acetate:" by W. H. Perkin, junr., and W. R. Hodgkinson.

XVI. "On the Determination of Nitrogen in Organic Bodies:" by C. E. Groves.

XVII. "On Essential Oil of Sage:" by M. M. P. Muir.

XVIII. "On the Presence of Nitrogen in Iron and Steel:" by A. H. Allen.

XIX. "On the Mode of Application of Pettenkofer's Process for the Determination of Carbonic Acid in Expired Air:" by W. Marcet.

XX. "Note on an Improved Form of Oven for Heating Sealed Tubes, and avoiding Risks of Explosions:" by Watson Smith.

XXI. "Note on a Convenient Form of Lead-bath for Victor Meyer's Apparatus for Determining the Vapour-densities of High-boiling Substances, together with a few slight Modifications:" by Watson Smith.

XXII. "On the Action of Air on Peaty Water:" by Lucy Halcrow and E. Frankland.

XXIII. "On the Spontaneous Oxidation of Organic Matter in Water:" by E. Frankland.

XXIV. "On Some Products of the Oxidation of Paratoluidine:" by W. H. Perkin.

XXV. "On the Detection of Foreign Colouring Matters in Wine:" by A. Dupré.

XXVI. "On the Action of Organo-zinc Compounds on Nitriles, and their Analogues. I. Action of Zinc-ethyl on Azobenzene:" by E. Frankland and D. A. Louis. II. "On the Action of Zinc-ethyl on Benzonitril:" by E. Frankland and J. Castell Evans.

XXVII. "On the Relation between the Molecular Structure of Carbon Compounds, and their Absorption Spectra:" by W. N. Hartley.

XXVIII. "On a Simple Method of determining Vapour-densities in the Barometer Vacuum:" by C. A. Bell and F. L. Teed.

XXIX. "On Pentathionic Acid:" by T. F. Takamatsu and Watson Smith.

XXX. "Preliminary Notes on some Orcinol Derivatives:" by J. Stenhouse and C. E. Groves.

XXXI. "On the Determination of Carbon in Soils:" by R. Warington and W. A. Peake.

XXXII. "Note on Camphydrene:" by H. E. Armstrong.

XXXIII. "On the Action of Nitric Acid on Diparatolylguanidine:" by A. G. Perkin.

XXXIV. "On Some Higher Oxides of Manganese and their Hydrates:" by V. H. Veley.

XXXV. "On a New Method of Preparing Dinitroethylic Acid:" by E. Frankland and C. C. Graham.

XXXVI. "On the Action of Organo-zinc Compounds upon Nitriles and their Analogues:" by E. Frankland and H. H. Tompkins.

XXXVII. "On the Action of Benzoyl Chloride on Morphine:" by C. R. A. Wright and E. H. Rennie.

XXXVIII. "An Examination of Terpenes for Cymene by means of the Ultra-violet Spectrum:" by W. N. Hartley.

XXXIX. "Note on the Purple of the Ancients:" by E. Schunck.

XL. "On a Crystal of Diamond:" by Harry Baker.

XLI. "On Dibromanthraquinones, and the Colouring-matters derived from them:" by W. H. Perkin.

XLII. "On the Formation of Amidosulphonic Acids by the Action of Concentrated Sulphuric Acid:" by R. H. C. Nevile and A. Winther.

XLIII. "On the Action of Ammonia and the Amines upon Naphthaquinone:" by R. T. Plimpton.

XLIV. "Experiments on Germinating Barley:" by T. Cuthbert Day.

XLV. "On Metallic Compounds containing Bivalent Hydrocarbon Radicals:" by J. Sakurai.

XLVI. "On the Action of Benzaldehyde on Phenanthraquinone, both alone and in presence of Ammonia:" by F. R. Japp.

XLVII. "On a New Boro-copper Compound of the formula B_2Cu_3:" by R. Sydney Marsden.

XLVIII. "Note on the Precipitation of Iron with Ammonium Succinate:" by Sydney Young.

XLIX. "On the Synthetical Production of Acids of the Pyruvic Series:" by C. L. Claisen and E. Moritz.

L. "Action of Heat on the Mixed Vapours of Benzene and Toluene. Two New Methylenediphenylenes:" by Thomas Carnelley.

LI. "On the Action of Benzyl Chloride on Phenyl Acetate," by W. H. Perkin, junr., and W. R. Hodgkinson.

LII. "On the Compounds of Vanadium and Sulphur:" by E. W. E. Kay.

LIII. "On the Atmospheric Oxidation of Phosphorus and some Reactions of Ozone and Peroxide of Hydrogen:" by C. T. Kingzett.

LIV. "On the Action of Organo-zinc Compounds on Nitriles and their Analogues. (Second Notice):" by E. Frankland and C. Colborne Graham.

LV. "Action of Zinc-ethyl on Benzoyl Cyanide:" by E. Frankland and D. A. Louis.

LVI. "On Bismuth and Bismuth Compounds:" by M. M. P. Muir, G. B. Hofmeister, and C. E. Robbs.

LVII. On the Colour-properties and Relations of the Metals, Copper, Nickel, Cobalt, Iron, Manganese, and Chromium:" by T. Bayley.

LVIII. "On the Action of Diazonaphthalene on Salicylic Acid:" by P. F. Frankland.

LIX. "On the Basic Sulphates of Iron:" by Spencer Pickering.

LX. "Fourth Report on Researches on Chemical Dynamics:" by C. R. A. Wright, E. H. Rennie, and A. E. Menke.

LXI. "On Some Naphthalene Derivatives:" by H. E. Armstrong and N. C. Graham.

LXII. "On the Manufacture of Caustic Soda from the Sulphate:" by Messrs. Bevan and Cross.

LXIII. "Acetylorthamidobenzoic Acid:" by P. P. Bedson.

LXIV. "Notes on the Oxides of Manganese:" by Spencer Pickering.

LXV. "On Aluminium Alcohols:" by J. H. Gladstone and A. Tribe.

LXVI. "On the Absorption-spectrum of Ozone:" by W. N. Hartley.

LXVII. "On the Probable Absorption of the Solar Rays by Atmospheric Ozone:" by W. N. Hartley.

LXVIII. "On the Synthetical Production of New Acids of the Pyruvic Series. (Part II):" by E. Moritz.

LXIX. "On the Ancient Alum-well of Harrogate:" by R. H. Davis.

LXX. "On Peppermint Camphor:" by M. Moriya.

LXXI. "On the Volumes of Sodium and Bromine at their Boiling Points:" by W. Ramsay.

LXXII. "On the Volume of Phosphorus at its Boiling Point:" by D. O. Masson and W. Ramsay.

LXXIII. "On the Specific Volume of Chloral:" by Laura Maude Passavant.

LXXIV. "Note on the Formation of Carbon Tetrabromide in the Manufacture of Bromine:" by J. C. Hamilton.

LXXV. "Researches on the Relation between the Molecular Structure of Carbon-compounds and their Absorption Spectra:" by W. N. Hartley.

LXXVI. "On a New Class of Colouring-matters from Phenols:" by Raphael Meldola.

LXXVII. On Nitroso-β-Naptholsulphonic Acids:" by Raphael Meldola.

LXXVIII. "On the Estimation of Nitrogen by Combustion, including Nitro-compounds:" by J. Ruffle.

LXXIX. "On Some Naphthalene Derivatives:" by H. E. Armstrong and N. C. Graham.

LXXX. "On the Effects of Pressure on some Fusing Points:"

LXXXI "On Pentathionic Acid:" by V. Lewes.

LXXXII. "A Preliminary Note on some Hydrocarbons from Resin Spirit:" by H. E. Armstrong.

LXXXIII. "On the Determination of the Relative Weight of Single Molecules:" by D. Vogel, of San Francisco.

LXXXIV. "On the Synthetical Production of Ammonia by the Combination of Hydrogen and Nitrogen in presence of Heated Spongy Platinum:" by G. S. Johnson.

LXXXV. "On the Oxidation of Organic Matter in Water:" by A. Downes.

LXXXVI. "Analysis of Queensland Soils:" by A. Liversidge.

LXXXVII. "On the Volumes of some Compounds of the Benzene, Naphthalene, Anthracene, and Phenanthrene Series:" by W. Ramsay.

LXXXVIII. "On a New Theory of the Conversion of Bar Iron into Steel by the Cementation Process:" by Dr. Marsden.

LXXXIX. "On the Action of Sulphydrate of Potassium on Chloral Hydrate:" by W. W. J. Nicoll.

XC. "On the Estimation of Organic Carbon in Air:" by A. Dupré and H. W. Hake.

XCI. "On the Action of the Copper-zinc Couple upon Nitrates and the Estimation of Nitric Acid in Water Analysis:" by M. W. Williams.

XCII. "On the Position taken by the Nitro-group on Nitrating the Dibromotoluenes:" by R. Nevile and A. Winther.

XCIII. "On Some of the Various Derivatives of Toluene and the Toluidines:" by R. Nevile and A. Winther.

XCIV. "On the Estimation of Organic Carbon in Water Analysis

simultaneously with the Estimation of Nitric Acid:" by M. W. Williams.

XCV. "On the Influence of the Molecular Grouping in Organic Bodies, on the Absorption in the Infra-red Region of the Spectrum:" by Captain Abney and Colonel Festing.

XCVI. "On the Absorption-bands in the Visible Spectrum produced by Certain Colourless Liquids:" by W. J. Russell and W. Lapraik.

XCVII. "On the Action of Hydrochloric Acid on Ethylene Alcohol:" by C. Schorlemmer.

XCVIII. "On an Attempt to accelerate the process of Determining the Soluble Salts in a Soil:" by E. W. Prevost.

XCIX. "On the Action of Bacteria on Various Gases:" by F. Hatten.

C. "On the Influence of Intermittent Filtration through Sand and Spongy Iron on Animal and Vegetable Matters dissolved in Water, and on the Reduction of Nitrates by Sewage:" by F. Hatten.

CI. "On River Water:" by C. M. Tidy.

CII. "On β-Diquinolyline:" by F. R. Japp and C. Colborne Graham.

CIII. "On the Volumes of Mixed Liquids:" by F. D. Brown.

CIV. "On Boron Hydride:" by F. Jones and R. L. Taylor.

CV. "On the Action of Aldehydes on Phenanthraquinone in Presence of Ammonia. (Second Notice):" by F. R. Japp and Edgar Wilcox.

CVI. "On the Action of Benzoic Acid on Naphthaquinone:" by F. R. Japp and N. H. J. Miller.

CVII. "Notes on the Appearance of Nitrous Acid during the Evaporation of Water:" by R. Warington.

CVIII. "On the Absorption of Solar Rays by Atmospheric Ozone and on the Blue Tint of the Atmosphere:" by W. N. Hartley.

CIX. "Note on the Sweet Principle of the *Smilax glycyphylla*:" by C. R. A. Wright and E. H. Rennie.

CX. "On New Zealand Kauri Gum:" by E. Rennie.

CXI. "On the Action of Mercury Nitrate on Alcohol:" by R. Cowper.

CXII. "On the Nature of Certain Volatile Products contained in Crude Coal-tar Benzenes:" by Watson Smith.

CXIII. "On Usnic Acid:" by C. E. Groves.

The following Officers were then announced from the chair as having been duly elected for the ensuing year:—

President.—H. E. Roscoe, LL.D., F.R.S.

Vice-Presidents who have filled the Office of President.—F. A. Abel, C.B., F.R.S.; Warren De La Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. Odling, M.B., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents.—A. Crum Brown, D.Sc., M.D.; J. Dewar, F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; A. V. Harcourt, F.R.S.; J. Emerson Reynolds, M.D., F.R.S.; J. Young, F.R.S.

Secretaries.—W. H. Perkin, F.R.S.; H. E. Armstrong, Ph.D., F.R.S.

Foreign Secretary.—H. Müller, Ph.D., F.R.S.

Treasurer.—W. J. Russell, Ph.D., F.R.S.

The other Members of the Council are—F. D. Brown, B.Sc.; M. Carteighe; H. McLeod; G. H. Makins; E. J. Mills, D.Sc., F.R.S.; W. C. Roberts, F.R.S.; C. Schorlemmer, Ph.D., F.R.S.; J. M. Thomson; C. Meymott Tidy, M.B.; W. Thorp, B.Sc.; T. E. Thorpe, Ph.D., F.R.S.; R. Warington.

APPENDIX.

FOURTH REPORT OF THE RESEARCH FUND COMMITTEE.

SINCE the last Anniversary Meeting, the following grants from the Research Fund have been made by the Council on the recommendation of this Committee:—

£10 to Mr. C. F. Kingzett, for experiments on the Oxidation of Phosphorus.

£25 to Mr. Watson Smith, for experiments on the Hydrocarbons Dinaphthyl, Phenylnaphthalene, &c.

£20 to Messrs. Bailey and Munro, for the study of certain Lactone-properties of Metals.

£20 to Professor Carnelley and Mr. O'Shea, for the determination of the Vapour-density of certain Compounds of Beryllium.

£20 to Dr. Hodgkinson, for the investigation of the Products of the Action of Sodium on certain Ethereal Salts of Phenylacetic Acid.

£6 to Dr. Marsden, for experiments on the production of Boron Hydride from a Boron-manganese Alloy.

£5 to Mr. J. T. Brown, for the construction of a Gas-density Apparatus.

During the year the following papers have been communicated to

the Society, describing the results of investigations for which grants have been made from the Research Fund:—

Dr. F. R. Japp: "On the Action of Organo-zinc Compounds on Quinones" (**37**, 408).

Dr. Thomas Carnelley: "On the Action of Heat on the Mixed Vapours of Benzene and Toluene" (**37**, 701).

Dr. Wright and Messrs. Rennie and Menke: "Fourth Report on Researches on some Points in Chemical Dynamics" (**37**, 757).

C. F. Kingzett: "Report on the Atmospheric Oxidation of Phosphorus" (**37**, 792).

Thomas Bayley: "On the Colour-properties and Relations of the metals Copper, Nickel, Cobalt, Iron, Manganese, and Chromium" (**37**, 828).

M. M. P. Muir and Messrs. E. B. Hoffmeister and E. C. Robb: "On Bismuth Compounds" (**37**, 21).

Drs. Dupré and Hake: "On the Estimation of Organic Carbon in Air" (**39**, 93).

Dr. Wright has communicated several papers to the Physical Society embodying the results obtained in the course of his research "On the Determination of Chemical Affinity in terms of Electromotive Force" (*Phil. Mag.* [5], **9**, 237, 331; **11**, 261).

At the last Meeting of the Society a paper was read by Mr. F. D. Brown "On the Volumes of Mixed Liquids;" and Mr. F. Jones, conjointly with Mr. Taylor, communicated the results of further observations on Boron Hydride. A paper "On the Organic Matter in Sea-water" will be read at the next Meeting of the Society by Mr. Jago.

The Committee have been favoured with reports from most of the gentlemen who have not yet communicated the results of researches for which grants have been made.

The condition of the Fund is shown in the appended Balance-sheet.

DR. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 20, 1880, TO MARCH 21, 1881. CR.

	£ s. d.	£ s. d.
Balance at Bank March 23rd, 1880	927 17 1	
,, in hand of Treasurer	2 0 3	
		929 17 4
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 19th, 1880, to March 21st, 1881.		
12 Life Compositions	240 0 0	
81 Admission Fees	324 0 0	
22 Subscriptions for 1878	44 0 0	
59 ,, ,, 1879	113 0 0	
227 ,, ,, 1880	446 0 6	
583 ,, ,, 1881	1,120 0 6	
		2,287 1 0
Sales of Journal	322 10 10	
Sale of Index	0 15 0	
		323 5 10
Subscriptions received for Proceedings of Royal Society		73 0 0
Received from Society of Public Analysts	3 0 0	
,, from Institute of Chemistry	7 0 0	
		10 0 0
Dividends on Consols (£4,000)	117 0 0	
,, Metropolitan Board of Works 3½ per cent. Stock	75 3 2	
,, London and North Western Railway Debenture Stock	30 15 2	
		222 18 4

Assets.	£ s. d.
Balance at Bank	1,204 18 0
,, in Treasurer's hands	0 4 0
Three per Cent. Consols	4,000 0 0
London and North Western Railway Debenture Stock	788 0 0
Metropolitan Board of Works 3½ per cent. Stock	2,200 0 0
	3,846 2 6

Expenses on Account of Journal.	£ s. d.	£ s. d.
Salary of the Editor	250 0 0	
,, Sub-Editor	100 0 0	
Fees to Abstractors of Papers	217 2 10	
Incidental expenses of Editor	4 0 0	
Periodicals for use of Abstractors	41 2 9	
Distribution of Journal	153 7 7	
Printing of Journal	922 18 8	
		1,688 11 10
Expenses on Account of the Library.		
Salary of Librarian	50 0 0	
,, Library Attendant	62 0 0	
Books, Periodicals, and Card Catalogues	222 0 1	
Binding Books and Periodicals	67 0 8	
Preparing New Catalogue, &c.	40 0 0	
		441 0 9
Printing Authors' Copies		38 16 7
Proceedings of Royal Society, vols. 29 and 30		80 0 0
Distributing the above		6 3 10
Reporting Meetings		24 0 0
Miscellaneous Printing		21 8 6
Insurance of Furniture and Books		2 0 0
Stationery, Postage, Envelopes, Receipt Books, &c.		33 4 4
Inhabited House and Income-tax		8 1 3
Legal Expenses		2 2 0
Collector's Commission on Subscriptions		114 7 0
Treasurer's Stamps, Cheque Book, and Clerical Aid		4 19 0
House Expenses.		
Providing Refreshments at Meetings	23 14 2	
Heating the Building	19 2 0	
Lighting ,,	50 15 10	
Cleaning ,,	20 0 0	
Wages of House Porter	47 14 0	
Petty House Expenses	8 17 9	
Fixing Ventilator, &c.	3 13 10	
Gratuity to Gate Porter	2 2 0	
		175 19 7
Treasurer's Petty Cash Disbursements		0 5 10
Balance in Bank	1,204 18 0	
,, in hands of Treasurer	0 4 0	
		1,205 2 0
		3,846 2 6

Examined and found correct, March 23rd, 1881. { FREDERIC JAS. M. PAGE, JOHN M. THOMSON, REG. C. WOODCOCK, } *Auditors.*

The Treasurer of the Chemical Society in Account with the Research Fund.

From March 23, 1880, to March 23, 1881.

Dr.

	£	s.	d.
Balance at Bank, March 23, 1880	152	8	11
Subscriptions and donations	257	7	0
Dividend on North British Railway Stock	39	2	3
„ Metropolitan 3½ per cent. Stock	102	9	9
	£551	7	11

Cr.

	£	s.	d.
July and August, 1880. By grants made	60	0	0
Feb. and March, 1881. By grants made	51	0	0
Jan. 28, 1881. By purchase of £300 Metropolitan Three and a-half per cent. Stock	313	2	6
March 21, 1881. By balance	127	5	5
	£551	7	11

Assets.	£	s.	d.
North British Railway 4 per cent. Preference Stock	1,000	0	0
Metropolitan Board of Works 3½ per cent. Stock	3,300	0	0
Balance at Bank	127	5	5

Examined and found correct, March 23, 1881,

Fred. Jas. M. Page,
John M. Thomson,
Reg. C. Woodcock,
} *Auditors.*

XXXI.—*Volume of Mixed Liquids.*

By Frederick D. Brown, B.Sc., Demonstrator in Chemistry at the University Museum, Oxford.

A chemical reaction generally results in the destruction of the original molecules which took part in the phenomenon, and in the construction of other molecules differing from the first, but containing the same atoms as they did. When the action of the chemical forces leaves the molecules intact, the chemist is apt to regard the whole matter as outside his special subject, and to leave the solution of the problems involved to the science of physics. The existence of double salts, however, of saline hydrates, of complex metallic oxides, and of polymeric substances, not only shows that a certain kind of action does take place between the molecules, but indicates that this action is of a chemical and not a physical character, a statement which is indeed abundantly proved by the more general facts of cohesion and solution.

In the various experiments on vapour-tension, fractional distillation, &c., upon which I have for some time been engaged, it has always been my chief object to learn something of this particular class of chemical phenomena in which the molecular encounters are not of an internecine character, and the present paper forms a small contribution to our knowledge of the subject.

It is undeniable that the molecules which make up the mass of a substance in the liquid or solid state are subject to mutual attraction, or to some combination of circumstances which assumes all the appearances of attraction; yet as the substance is capable of occupying a smaller volume, it would seem that the molecules cannot be quite close together, but must, as regards their mean distances from each other, be in a position of equilibrium liable to change when the forces which solicit them change. This being the case, the mean distances between the molecules must, *cæteris paribus*, increase when the energy of attraction diminishes, and diminish when that energy increases; and this must be true whether the particles concerned are in motion or at rest, provided that if they are in motion, their mean velocity does not vary. The study of these mean distances may therefore afford some clue to the nature and value of these attractions. As regards the absolute distances, we are much in the dark; but viewed relatively, they are not so entirely beyond our ken, the molecular volumes of substances furnishing us with their approximate measure. These volumes refer exclusively to the forces exerted between similar molecules, whereas

I have been chiefly anxious to obtain information regarding the interaction of dissimilar molecules.

I was led to make the experiments recorded below by the necessity of ascertaining with perfect certainty and with tolerable facility the composition of any given mixture of two liquids. The density of the mixture was evidently among the most readily accessible of those of its properties which varied with its composition, and I therefore determined to make use of it for the above-mentioned object. As I was uncertain whether the true density of a mixture was the same as that calculated from the densities and relative weights of the liquids mixed, I added several liquids to each other in pairs; and on measuring the densities of the resulting mixtures, was astonished to find that in the majority of cases a considerable *expansion* took place. In a few others there was a similar contraction; while in only one of the cases then roughly studied could the two liquids be mingled without appreciable change of volume. On further inquiry, I learnt that the same facts had been observed by MM. Bussy and Buignet (*Compt. rend.*, **59**, 673; and **64**, 330), but their probable importance in elucidating the laws of molecular action induced me to subject them to exact measurement.

The necessity of considerable accuracy was immediately apparent, the object of measurement being a small change of volume, the value of which was to be given by the ratio of two densities differing but little one from the other. It was therefore evident that a small error in one of these densities would produce a very considerable one in the value of the change of volume. Thus, if V = the volume, D = the true density of a mixture, and V_1 = the calculated volume, *i.e.*, the sum of the volumes of the liquids before mixing, D_1 = the calculated density, C = the change of volume which the unit volume of unmixed liquids undergoes, we have

$$C = \frac{V - V_1}{V_1} = \frac{D_1 - D}{D}$$

If the value of D be subject to an error ϵ, the value of C will be subject to an error which will give it another value C', and we shall have

$$C' = \frac{D_1 \pm \epsilon - D}{D \pm \epsilon}$$

if $D_1 - D = 0{\cdot}001$, we have

$$C' = \frac{\pm \epsilon\ 0{\cdot}001}{D + \epsilon}, \text{ whereas } C = \frac{0{\cdot}001}{D},$$

whence it is evident that if ϵ equals an error in the determination of the density of 1 in the fourth place of decimals, an error of 10 per

cent. will be made in the estimation of C', and where D_1 and D are still nearer together, the value C may appear negative instead of positive, and *vice versâ*. In order to avoid all possible sources of error, special precautions were taken—(1) Regarding the temperature of the liquid; (2) regarding its volume; (3) regarding its weight.

(1.) One thermometer was used throughout the experiments; it was a so-called "standard" thermometer, each degree of which was 7 mm. long, and was divided into 10 parts; the hundredth of a degree could therefore be fairly estimated. During the experiments this thermometer was used for no other purpose, and it was therefore never heated much above 20°; its zero consequently was not subject to sudden variation. In order to diminish as much as possible this displacement of the zero, the thermometer was placed in a brass tube, through which a current of steam could be passed. Steam was then passed through this tube for about ten minutes at intervals of half an hour, the thermometer being alternately heated to 100° and cooled to about 30°; and this process was continued for several days, the thermometer being heated to 100° more than one hundred times in succession. This has been found by those intimately acquainted with the subject to be the most effectual way of preventing subsequent displacement of the zero. During the experiments the zero was observed from time to time in melting ice, and any alteration in its position was allowed for. The thermometer was further compared with the standard mercurial thermometers employed in all my experiments, and a correction made for the error of its reading at 20°. The temperature 20° mentioned below is therefore always exactly the same, and is as nearly as possible the true temperature of 20° as measured by an ideal mercurial thermometer.

The **U**-tubes (Dr. Sprengel's form) in which the densities were taken were immersed in about 2 litres of water, constantly stirred by means of a small electromotor and contained in a copper cylinder, which was surrounded by a copper jacket filled with water, the outer jacket being separated from the inner cylinder by a space one centimeter broad; by a sufficiently long immersion the liquid in the tubes acquired the temperature of the surrounding water with great exactitude. The method of making the experiments and other details was described by me in this Journal (1879, p. 551).

(2.) The capacity of the tubes was obtained by weighing the water which filled them with the same precautions as to temperature. This was done several times and the mean taken, it being found that at 20° one of the tubes called P contained 13·8892 grams, while the other, Q, contained 13·2926 grams; these numbers were frequently verified during the experiments. Throughout the whole time which these lasted, the tubes were never heated above 40°, as it had been found

that if they were much heated, they possessed on cooling a considerably increased capacity.

(3.) The weighings were made on a first-class balance capable of indicating with ease variations of one-tenth of a milligram. Corrections for the displaced air were not made, it being easily demonstrated that such corrections cannot materially influence the values obtained for the change of volume which takes place on mixing.

The first pairs of liquids selected for experiment were those which I have used for fractional distillation, viz. :—

Carbon disulphide and benzene.

Carbon disulphide and carbon tetrachloride.

Carbon tetrachloride and benzene.

Carbon Disulphide and Benzene.

The methods employed for the purification of these liquids, together with the results obtained with them, are given in the paper before referred to. The experiments were made at 19·80°, but as they were all made at the same temperature, this does not influence the numbers. The percentages of CS_2 being taken as abscissæ, and the expansions $\frac{D}{D_0} - 1$ as ordinates, the points marked (a) on the accompanying diagram were obtained; a curve was then drawn, representing as nearly as possible the locus of these points. It will be observed that as these were the first experiments made, the position of the points leaves much to be desired. As the printed curve does not admit of accurate measurement, I append the value of the ordinates for every 10 per cent. of CS_2, the percentage being the number of molecules of CS_2 out of every 100 present.

Percentage of CS_2.	Change of volume.	Percentage of CS_2.	Change of volume.
0	+ 0·0000	60	+ 0·0082
10	+ 0·0022	70	+ 0·0072
20	+ 0·0041	80	+ 0·0057
30	+ 0·0058	90	+ 0·0034
40	+ 0·0072	100	+ 0·0000
50	+ 0·0082	—	—

Carbon Tetrachloride and Carbon Disulphide.

The carbon tetrachloride employed was purchased. A quantity was mixed with a little antimony pentachloride, and chlorine was passed through it in the sunlight; it was then shaken with water, and distilled

twice with steam; finally it was shaken with dilute soda, then with concentrated sulphuric acid, over which liquid it was finally rectified. Subjected to fractional distillation, the larger portion came over between 76·4 and 76·5 (uncorr.); this was the portion employed in the subsequent experiments. Its density at 20° referred to water at 20° was repeatedly found to be 1·59742. The carbon disulphide was purified as in the abovementioned case, and its density (mean of 3 experiments) found to be 1·26583. Mixtures were now made of the two liquids in different proportions, and their densities measured; the details of these observations are given in the following table. It will be observed that the actual temperatures at which the densities were taken differ slightly from 20°; the correction c applied to the densities was given by the formula—

$$c = \theta \times D \times 0{\cdot}000012,$$

where θ equals the number of hundredths of a degree which the temperature differs from 20°, being reckoned positively where the temperature is greater, and negatively where it is less than 20°; D is the density observed; the quantity 0·000012 is derived from the experiments of Pierre, on the expansion of carbon tetrachloride and carbon disulphide; both substances expand at about equal rates at 20°; the density D_1 at 20° becoming $D_1 - (D_1 \times 0{\cdot}000012)$ at 20·01°.

No. of mixture.	Weight of CCl_4.	Weight of CS_2.	Per cent. of CCl_4 in mols.	Density as found.	Temp. at which D taken.	Density corrected to 20°.	Calculated density.	Calculated Density. True density.
I.	15·606	70·570	9·840	1·31272	19·98	1·31269	1·31527	1·00197
II.	15·538	31·709	19·474	1·35433	19·98	1·35430	1·35857	1·00315
III.	23·757	27·782	29·676	1·39435	19·97	1·39430	1·39976	1·00391
IV.	31·810	23·573	39·974	1·43117	19·91	1·43102	1·43718	1·00430
V.	31·686	15·652	49·976	1·46426	19·91	1·46410	1·47009	1·00409
VI.	32·025	10·910	59·161	1·49223	19·96	1·49216	1·49773	1·00373
VII.	31·852	6·808	69·779	1·52219	20·07	1·52232	1·52698	1·00306
VIII.	63·315	7·699	80·231	1·55012	19·96	1·55005	1·55331	1·00210
IX.	71·168	4·577	88·471	1·57057	20·00	1·57057	1·57253	1·00125

The numbers in the fourth column were calculated by means of the formula—

$$x = \frac{100 \times \frac{W_1}{154}}{\frac{W_1}{154} + \frac{W_2}{76}}$$

where W_1 and W_2 are the weights of CCl_4 and CS_2 respectively. Those in the eighth are, of course calculated by means of the formula—

$$D = \frac{W_1 + W_2}{\frac{W_1}{D_1} + \frac{W_2}{D_2}}$$

where D_1 and D_2 are the densities of CCl_4 and CS_2 respectively.

It will be noticed that a considerable expansion, amounting at 40 per cent. to 0·0043, takes place on mixing these liquids. The numbers given in the ninth column are recorded on the diagram, and the points obtained are marked (*b*). They all lie well on the curve, the accuracy of the experiments being greatly superior to those made with carbon disulphide and benzene. The expansion as measured from the curve for every 10 per cent. of CCl_4 is given in the following table:—

Percentage.	Expansion.	Percentage.	Expansion.
10	+ 0·00197	60	+ 0·00367
20	+ 0·00320	70	+ 0·00302
30	+ 0·00395	80	+ 0·00212
40	+ 0·00429	90	+ 0·00111
50	+ 0·00410	100	+ 0·00000

Carbon Tetrachloride and Benzene.

The samples of these substances employed in the experiments were not the same as those previously used, but they were purified in the same manner. The densities were—

$D_1 = 1·59742$ and $D_2 = 0·88038$ respectively.

The following table, corresponding exactly with that above given, resumes the data of all the experiments:—

No. of mixture.	Weight of CCl_4.	Weight of C_6H_6.	Per cent. of CCl_4 in mols.	Density as found.	Temp. of observation.	Density corrected to 20°.	Calculated density.	Calculated density. True density.
I.	15·223	73·546	9·489	0·95388	20·00	0·95388	0·95380	0·999918
II.	15·469	32·412	19·467	1·02983	20·00	1·02983	1·02971	0·999880
III.	23·635	28·726	29·415	1·10433	19·96	1·10420	1·10408	0·999813
IV.	31·734	24·653	39·563	1·17829	19·96	1·17825	1·17796	0·999751
V.	32·035	16·502	49·578	1·25117	20·03	1·25120	1·25101	0·999845
VI.	31·439	10·951	59·252	1·32001	20·03	1·32004	1·31974	0·999770
VII.	47·595	10·438	69·784	1·39363	20·00	1·39363	1·39331	0·999770
VIII.	63·108	8·173	79·637	1·46116	20·00	1·46116	1·46099	0·999881
IX.	110·785	6·286	89·926	1·53066	19·96	1·53059	1·53049	0·999934

The corrections c for the seventh column were made as formerly, but using the expression—

$$c = \theta \times D \times 0{\cdot}000011,$$

such being the mean correction for benzene and carbon tetrachloride. The numbers given in the ninth column are recorded on the diagram; the points obtained are marked (e), all of which lie practically on the curve. The contraction as measured from this curve is given for every 10 per cent. of tetrachloride in the following table:—

Percentage.	Contraction.	Percentage.	Contraction.
10	− 0·00010	60	− 0·00021
20	− 0·00014	70	− 0·00020
30	− 0·00020	80	− 0·00013
40	− 0·00024	90	− 0·00008
50	− 0·00022	100	− 0·00000

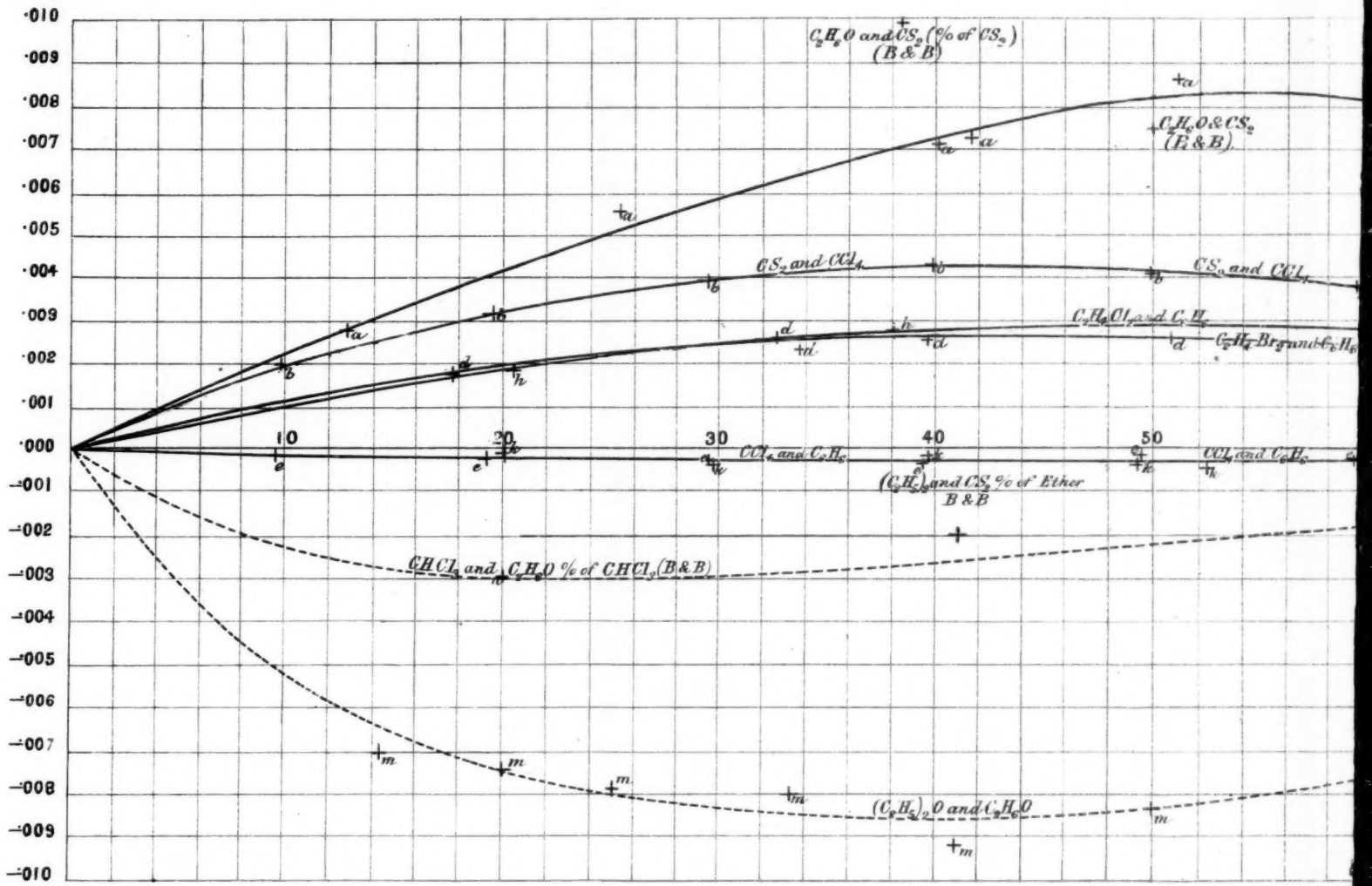
A very small contraction takes place, therefore, on mixing these two liquids.

Thus far the liquids selected for the experiments had no special reference to the subject, the only point being that they had no apparent action one upon the other. Two of the pairs expanded considerably; the third was subject to slight contraction. Let us before going further, look at the results obtained by MM. Bussy and Buignet. They are as follows:—

	Maximum change.
Ether and carbon disulphide	− 0·002
Alcohol and chloroform	− 0·003
Alcohol and carbon disulphide	+ 0·010
Chloroform and carbon disulphide.....	+ 0·006
Alcohol and ether.....	− 0·0086

The results given by these philosophers are marked on the diagram as well as possible, the points being accompanied with their signification, and by the letters (B and B). In the case of alcohol and chloroform, and more especially in that of alcohol and ether, where the experiments are given in greater detail, I have drawn curves (in dotted lines), representing as nearly as possible the contractions which take place. In the case of alcohol and carbon disulphide, no curve of the same general form as the others will pass through the two points given:—

Looking at all these results together, we can form no idea of the circumstances under which a positive or negative change of volume may be produced, the only point on which the slightest stress can be



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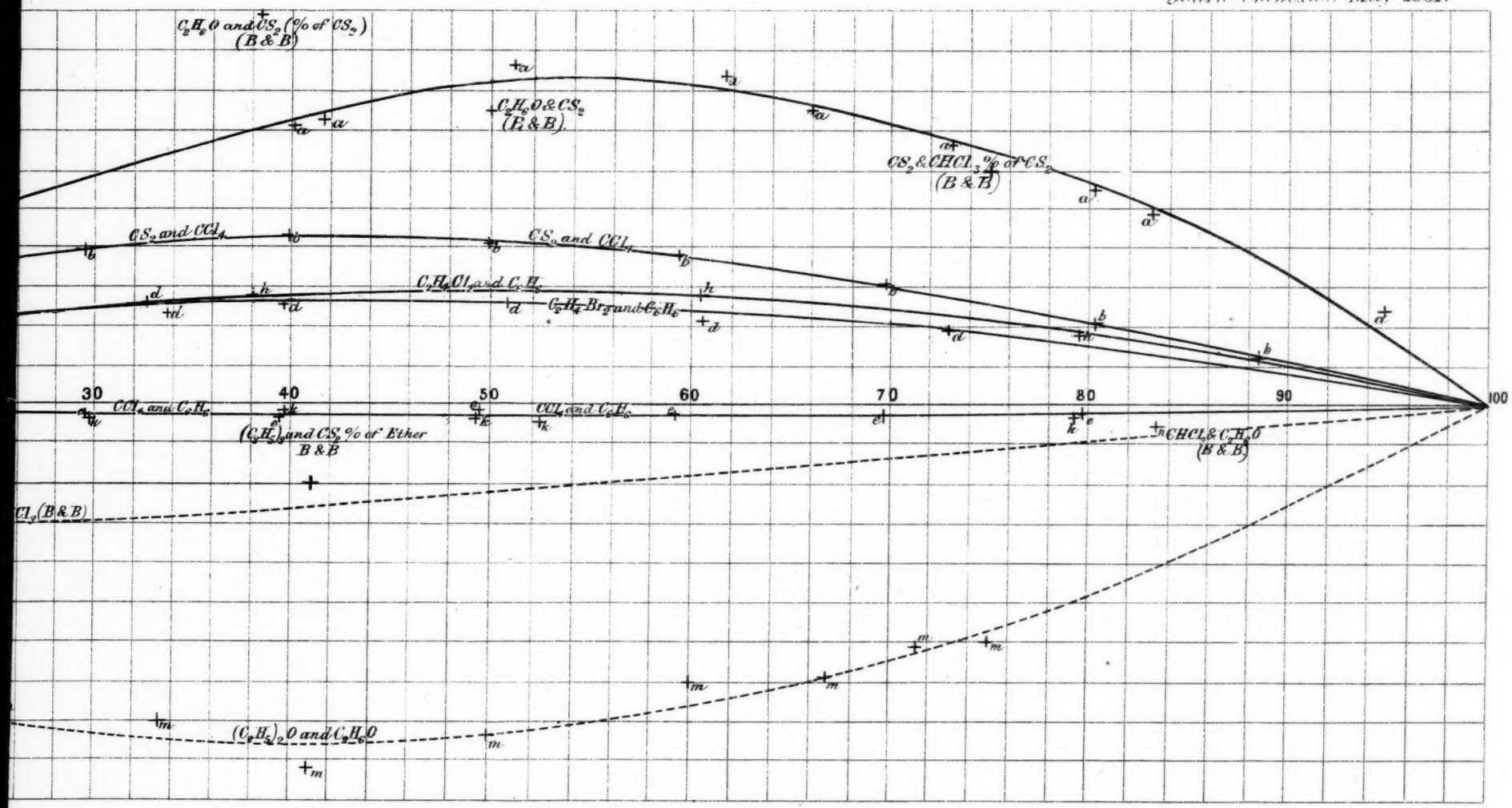
VOLUME OF MIXED LIQUIDS.

Journ. Chem. Soc. May 1881.



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laid is that alcohol generally produces a contraction, but even this is not always the case. Seeing that any number of pairs of liquids might be mixed together, and no better results obtained, I endeavoured to find under what conditions a change of volume was wanting. It seemed to me, arguing from the instance of C_6H_6 and CCl_4, that this might be when the vapour-tensions of the two liquids were nearly the same. The vapour-tensions of these two liquids at 20° are given by Regnault as 76 mm. for benzene, and 91 mm. for carbon tetrachloride; they are therefore not very far apart, and this hypothesis was supported by the fact that in the case of ether and carbon disulphide, the tensions of the vapour of which at 20° are 433 mm. and 298 mm. respectively, the contraction observed was comparatively small.

In order to see whether this supposition was of any value, I mixed dichlorethane with benzene. The vapour-tension of the former substance was not measured by Regnault, but its boiling point is about 84°, as compared with 80° for benzene.

Dichlorethane and Benzene.

The dichlorethane was purchased of Kahlbaum, a kilogram being obtained; it was treated with caustic potash, and then with sulphuric acid, in both cases without heating. The whole quantity afterwards distilled between 83° and 85°, but the greater portion came over between 84° and 84·5°. This fraction was used for the experiments. Its density at 20·00° was found to be $D_1 = 1{\cdot}25105$. The density of the sample of benzene employed, which had been purified in the usual manner, was $D_2 = 0{\cdot}88036$.

The following table gives the experiments, with the results obtained. The correction c applied to the members of the fifth column; to obtain those of the seventh was $c = \theta \times D \times 0{\cdot}000011$:—

No. of mixture.	Weight of $C_2H_4Cl_2$.	Weight of C_6H_6.	Per cent. in mol. of $C_2H_4Cl_2$.	Observed density.	Temp. of observation.	Density corrected to 20°.	Calculated density.	Calculated density. / True density.
I.	5·295	16·200	20·478	0·94767	20·20	0·94790	0·94968	1·00188
II.	13·893	16·351	40·100	1·01598	20·20	1·01622	1·019·6	1·00280
III.	20·558	10·587	60·473	1·09124	20·12	1·09139	1·09440	1·00276
IV.	27 272	5·533	79·523	1·16570	20·12	1·16587	1·16809	1·00191

The four experiments gave the four points marked (h) on the diagram. As they all lie fairly on the curve drawn, I thought it unnecessary to increase the number of observations.

Inspection of this curve shows that the hypothesis that liquids

having the same boiling point mix together with little or no change of volume, must be rejected.

I now sought the effect of mixing together two liquids, of which the molecular volumes, or volumes occupied by their gram molecules, were approximately equal, but of which the boiling points were widely different. For this purpose I selected dibromethane and benzene, the molecular volumes of which at 20° are about 88·6 and 86·6 respectively, while the boiling points are 80° and 131°, or thereabouts.

Dibromethane and Benzene.

The benzene was the same as that employed in the above mixtures, its density being $D_2 = 0{\cdot}88036$. The dibromethane was purchased of Kahlbaum, and was purified by means of caustic potash and sulphuric acid in the same way as the chlorine compound. The endeavour to obtain the pure substance was not, however, very successful, the liquid always beginning to give off acid fumes after a certain lapse of time. On distillation it all passed over between 129·2° and 131·4° (uncorr.). The portion distilled between 129·6 and 130·1 had a density at 20°—$D_1 = 2{\cdot}17053$. The portion distilling between 130·1 and 131·4 had a density $D_1 = 2{\cdot}17626$.

In the table given below, those mixtures which are marked with an asterisk were made with the first sample, the others with the second. The expansion of dibromethane at 20° as given by Prof. Thorpe, is very nearly the same as that of benzene, the correction c, therefore, was taken as having the value $c = \theta \times D \times 0{\cdot}000010$.

The following table gives the results as in the previous cases:—

No. of mixture.	Weight of $C_2H_4Br_2$.	Weight of C_6H_6.	Per cent. in mol. of $C_2H_4Br_2$.	Observed density.	Temp. of observation.	Corrected density.	Calculated density.	Calculated density. True density.
*I.	32·867	13·199	50·815	1·52438	20·19	1·52467	1·52864	1·00260
*II.	43·543	6·682	72·939	1·81275	20·01	1·81277	1·81638	1·00199
*III.	22·396	19·114	32·711	1·29268	20·01	1·29·69	1·29597	1·00254
*IV.	19·738	11·443	41·713	1·40775	20·01	1·40776	1·41142	1·00260
*V.	11·488	22·009	17·801	1·10383	20·01	1·10384	1·10577	1·00175
VI.	33·195	8·946	60·622	1·65465	19·97	1·65460	1·65811	1·00212
VII.	22·123	17·884	33·916	1·30946	19·97	1·30942	1·31256	1·00240

The points representing the above results on the diagram are marked with the letter (d). The curve passes through the points given by the first five experiments, but it is important to notice that the other two, in which a different sample of the bromide was employed, lie but little below it; hence it may be inferred that good numerical results may be obtained without using substances of excessive purity. It should,

however, be noted that this comparative harmlessness of a little foreign substance applies only to substances of the same general nature; it would be wrong to assert that the presence of traces of water, for instance, would not seriously interfere with the confidence to be placed in the numbers. The above table shows that expansion takes place when dibromethane and benzene are mingled together, hence the idea that substances whose gram-molecules occupied nearly the same space would mix without change of volume, is also to be rejected.

On examining the various curves, it will be noticed that the expansion in the case of dibromethane is practically the same as in that of dichlorethane; here, then, we have another possible solution of the difficulty, viz., that the expansion depends entirely on the *chemical* characters of the substances, and not in any way on their *physical* properties, for it is manifest that dibrom- and dichlor-ethane, though similar chemically, are widely different physically. In order to test this assumption, carbon tetrachloride was mixed with toluene, with a view to comparing the results with those obtained with carbon tetrachloride and benzene.

Carbon Tetrachloride and Toluene.

The carbon tetrachloride was purified; as in the previous cases, its density (resulting from many observations) was found to be $D_1 = 1{\cdot}59712$. The whole boiled between 76·45 and 76·60 (uncorrected). The toluene was the purest which could be purchased; before using it, it was digested with sodium for several days, and finally rectified over sodium. On subjecting it to fractional distillation all but an insignificant fraction distilled between 110·9° and 111·2° (uncorrected). The density of this liquid at 20° was found to be $D_2 = 0{\cdot}86684$ (mean of four experiments).

The following table gives the numbers obtained with eight mixtures. The correction c being taken as equal to $\theta \times D \times 0{\cdot}000011$,

No. of mixture.	Weight of CCl_4.	Weight of C_7H_8.	Per cent. of CCl_4	Observed density.	Temp. of observation.	Corrected density.	Calculated density.	Calculated density. / True density.
I.	9·922	23·592	20·080	1·00260	20·04	1·00265	1·00256	0·99991
II.	12·894	18·173	29·769	1·07007	20·05	1.07013	1·06988	0·99976
III.	17·618	15·897	39·834	1·14124	20·05	1·14130	1·14113	0·99985
IV.	25·798	15·748	49·460	1·21054	20·27	1·21090	1·21055	0·99971
V.	23·873	12·987	52·339	1·23176	20·20	1 23203	1·23156	0·99962
VI.	25·414	10 351	59·406	1·28404	20·27	1·28442	1·28277	0·99872
VII.	—	—	—	—	—	—	—	—
VIII.	51·046	7·963	79·294	1·43416	20·20	1·43447	1·43408	0·99973

the latter value being derived from experiments on the thermal expansion of toluene of Louguinine and of CCl_4 of Pierre.

The points representing the above results on the diagram are marked with the letter (*k*). The curve which would represent the locus of these points is so near the corresponding curve for benzene and CCl_4, that I thought it better in order to avoid confusion not to draw it. The numbers form a remarkable confirmation of the supposition that these changes of volume are dependent on the chemical character of the molecules, and entirely independent of such physical properties as the vapour-tension, molecular volume, &c. In order to afford further support to this view, it would be well to make experiments with other homologues and similar substances, such as CCl_4 and xylene, CS_2 and toluene, CS_2 and xylene, and so on. The expansion taking place on mixing carbon disulphide and chloroform is, according to MM. Bussy and Buignet, much greater than that which occurs in the case of carbon disulphide and carbon tetrachloride; but as has been previously remarked, the numbers given in the former case cannot be entirely correct. The difference in these two cases cannot therefore be cited as an objection to the above view.

I cannot but think that the facts now brought forward will, when further developed, prove to be of considerable importance; it seems impossible to reconcile them with the ordinary conceptions regarding the molecular condition of solutions. That the general equilibrium should be undisturbed when molecules of toluene weighing 92 replace those of benzene weighing 78 appears to me most extraordinary, unless we suppose that the molecules of a liquid are really close together. It would, however, be useless to discuss such a question as this at the present stage of the inquiry.

The fact that the mixture of two liquids without apparent action one upon the other generally results in an increase of volume is also very remarkable. One would be inclined to think that the result was brought about by the comparatively small mutual attraction of the dissimilar molecules. Thus if A and B be molecules of two liquids, and the attractions between A and A and between B and B are greater than those between A and B, the mean attraction would be lessened on mingling, and therefore the molecules would move further apart, but in this case it is difficult to see why the two liquids should mix at all.

The above experiments are all made at 20°. It would be interesting to know what change would take place in the curves if the temperature of observation were changed. From the experiments of Mendelejeff and of Dupré and Page on mixtures of alcohol and water, it would seem probable that the change of volume would be less marked at higher temperatures. Experiments in this direction in-

volve unfortunately an amount of labour out of all proportion to the probable value of the results.

The thermal change which accompanies the mixing of two liquids was the question more specially studied by MM. Bussy and Buignet, but no general law of any kind could be detected. Should this field of investigation fail to attract other labourers, I shall endeavour to find an opportunity for a few experiments upon it.

XXXII.—*On Boron Hydride.*

By Francis Jones, F.R.S.E., and R. L. Taylor.

The existence of a hydride of boron has already been pointed out by one of us in a preliminary note (*Chem. Soc. J.*, Trans., January, 1879), and we now propose to lay before the Society the results of the further examination of this compound. That a hydride of boron might be prepared appeared highly probable from various considerations; first, the fact that all the other metalloids form compounds with hydrogen; second, the discovery by Buff and Wöhler in 1857 of the hydride of the closely analogous element silicon; and further, the discovery by Frankland of the compounds of boron with methyl and ethyl.

The method used by Buff and Wöhler for the preparation of silicon hydride is well known. By acting on potassium silicofluoride with magnesium they obtained magnesium silicide, which on treatment with an acid yields the hydride. It appeared possible that a similar process (with substitution of borofluoride for silicofluoride) would yield magnesium boride, but, as already mentioned in the preliminary note, this reaction was tried and failed, and the methods finally adopted were the following:—

Preparation of Magnesium Boride.

Method A. By Action of Magnesium on Boric Anhydride.—Boric anhydride recently ignited is finely powdered and intimately mixed with not less than twice its weight of magnesium dust. The mixture is placed in a hessian or iron crucible, the lid of which is firmly wired down, and heated in an ordinary fire. Repeated experiments showed that no better product was obtained by using more than the above proportion of magnesium, which corresponds nearly with that required by the equation—

$$B_2O_3 + 6Mg = B_2Mg_3 + 3MgO.$$

When the proper temperature is reached the reaction takes place almost with explosive violence, particularly if the boric anhydride has not been thoroughly ignited. Immediately after the reaction the crucible is removed from the fire and allowed to cool. The residue is by no means a pure product; it contains boron and magnesium, together with boride, nitride, and oxide of magnesium. The quantity of nitride increases if the crucible be left in the fire after the reaction has taken place; indeed in some experiments in which this was the case it was the chief product. It was also ascertained that there was no advantage in employing a temperature higher than that of an ordinary fire.

The residue found in the crucible is chiefly a grey friable mass; some portion, however, has a fused appearance, and adheres closely to the crucible and lid. When strong hydrochloric acid is dropped on it, the gas evolved frequently takes fire spontaneously. This is particularly the case with the portion adhering to the crucible, and is doubtless due to some extent to the presence of magnesium silicide. The spontaneous inflammability is most marked when a new crucible is used, but that it is not entirely due to the presence of the silicide was proved by the same result occurring when an iron crucible had been employed.

Method B. By direct Union of Boron with Magnesium.—Amorphous boron is thoroughly mixed with rather more than thrice its weight of magnesium dust, and heated in a current of hydrogen or in a closely covered crucible lined with magnesia. At a dull red heat combination takes place, the mixture glows and need not be further heated, but is allowed to cool in a current of hydrogen. The product is darker in colour than that obtained by the preceding method.

Method C. By Action of Magnesium on Boron Trichloride.—Magnesium dust contained in a porcelain boat is placed in a combustion tube connected with a small retort containing boron trichloride. After the air has been expelled from the apparatus by a current of hydrogen, the boron trichloride is gently heated, and its vapour led over the magnesium, which is also heated. Great heat is evolved by the reaction, the magnesium glows brightly, and an almost black compound is produced on the surface, but the lower layer always contains unaltered magnesium. The reaction is represented by the following equation:—

$$6Mg + 2BCl_3 = B_2Mg_3 + 3MgCl_2.$$

The presence of magnesium chloride causes the product to deliquesce somewhat rapidly on exposure to the air.

Although methods B and C appeared to yield a slightly better product than the first method, they were not generally used, as the sub-

stance could be much more conveniently obtained in quantity by method A.

Preparation of Boron Hydride.

The most convenient way for preparing the gas from the magnesium boride obtained by any of the above methods, is to place it along with a little water in a small flask provided with a stoppered funnel tube, in which strong hydrochloric acid is placed. The acid is allowed to drop gradually on the contents of the flask, when a rapid evolution of gas occurs, and the mixture becomes hot and froths up considerably. The gas, though slightly soluble, may be collected over water, or may be dried over calcium chloride and collected over mercury. When all reaction ceases, the insoluble residue in the flask consists of amorphous boron, which when washed and dried may conveniently be used for the preparation of magnesium boride by method B.

The gas obtained in this way contains boron hydride mixed with a very large excess of hydrogen, and we have unfortunately not yet discovered any process which will yield the hydride in anything like a state of purity. When then we speak of "the gas," it must be understood that the mixture of boron hydride with hydrogen is referred to.

Properties of the Gas.

The gas obtained as above is colourless, and has an extremely disagreeable and very characteristic odour, producing nausea and headache even when inhaled in moderate quantity. It is sparingly soluble in water, to which it imparts its peculiar odour; the solution is apparently unaltered by keeping, some of it having been kept for two years without any appreciable alteration. The gas burns with a splendid green flame, producing boric acid by its combustion. This is well shown by the green tinge imparted to a Bunsen lamp flame held above a burning jet of the gas. When observed through the spectroscope, the flame of boron hydride exhibits the characteristic green boron lines.

Like the hydrides of arsenic and antimony, the gas is decomposed by passing through a red-hot tube, boron being deposited as a brown film, and if the gas at the extremity of the tube be kindled, it no longer burns with a green flame. The temperature required for the decomposition is somewhat higher than in the case of arsine and stibine. When a cold porcelain plate is held in a burning jet of the gas, boron is deposited as a brown film.

Solution of silver nitrate is decomposed when the gas is bubbled through it, a black precipitate being produced which contains both boron and silver. This precipitate is rapidly formed at first, but the

reaction soon ceases, the liberated nitric acid appearing to prevent further decomposition. With ammonio-nitrate of silver no better result was obtained. The black precipitate is slightly soluble in water, and is decomposed by hot water with liberation of boron hydride. For these reasons it was difficult to obtain a sufficient quantity of the compound for accurate analyses. Two determinations gave respectively 93·11 and 94·4 per cent. of silver. The boron was not determined, but its presence in the compound was ascertained by qualitative reactions.

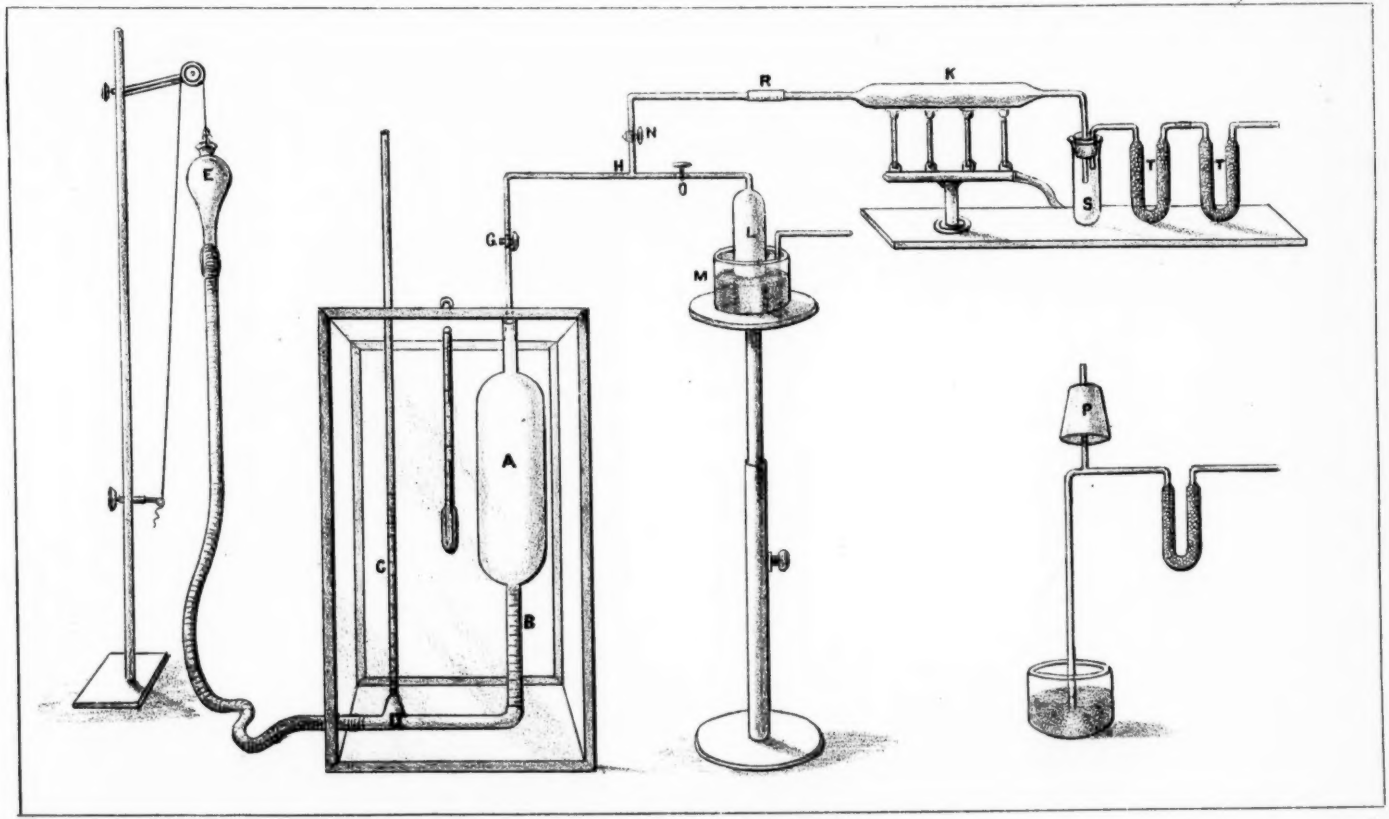
Boron hydride decomposes solution of potassium permanganate with separation of oxide of manganese, and formation of boric acid.

Action of Boron Hydride on Ammonia.

The compounds of boron with ethyl and methyl were found by Frankland to combine directly with ammonia, and it would seem that boron hydride behaves in a somewhat similar manner. The gas was passed for some time through strong ammonia contained in a **U**-tube, which was immersed in a freezing mixture. The escaping gas at once lost the characteristic smell of boron hydride, but possessed a peculiar fœtid odour, and burned with a yellowish-green flame. A slight crystalline deposit was noticed in the **U**-tube, which disappeared on heating. The ammonia solution when treated with an acid lost the peculiar fœtid odour, but regained the smell of boron hydride. A portion of it was evaporated in a vacuum, and a very small quantity of crystalline substance remained, which had an alkaline reaction, and when heated in a dry tube gave a white sublimate. A fused residue remained which tinged the lamp-flame green, and was doubtless boric acid. The crystalline substance when warmed with pure soda evolved ammonia, and when dissolved in water gave with silver nitrate a black precipitate, soluble in nitric acid. In order to prepare even this small quantity of the ammonia compound, so large a volume of gas was required that we despaired of preparing it in quantity sufficient for a more complete examination or for analysis.

Composition of the Gas.

All efforts to obtain the hydride in a state even approaching to purity having failed, we attempted to ascertain its composition by analysing the mixture of it with hydrogen. So small is the proportion of hydride present in the mixture that an ordinary eudiometric analysis is useless, and it was clearly necessary to employ a comparatively large volume of gas for the determination. For this purpose we had an apparatus specially constructed, which is represented in the



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accompanying sketch. It will be seen that this is practically a modification of Frankland's gas analysis apparatus, differing from it chiefly in the greater capacity of the gas-measuring vessel A, which, instead of being immersed in water, is enclosed in a closely fitting box with glass sides; we found this arrangement served the purpose perfectly well.

The gas is measured in the pipette-shaped glass vessel A, which is graduated at B, and has a capacity of about 700 c.c. Below B the tube is bent at right angles, and from it passes an upright tube C, also graduated in millimeters. The open end of the tube D is connected with a flexible tube attached to a mercury reservoir E, which can be raised or lowered at pleasure. The upper end of A terminates in a capillary tube, which can be closed with the glass stopcock G, and is further connected with the two-way tube H, so as to communicate either with the combustion-tube K or the laboratory tube L, which dips into the mercury trough M.

In using the apparatus, mercury is first poured into E (all the stopcocks being open), and when it reaches G, the stopcock N is closed, and the reservoir lowered until the laboratory tube L is full of mercury. O is then closed, N is opened, and the reservoir E raised to its former level; when the mercury reaches the stopcock N it is closed, and the whole apparatus thus becomes filled with mercury. The thoroughly dried gas is now bubbled up into L, and drawn over into A by lowering E, the stopcocks O and G being open. When the gas reaches B, G is closed, and the trough M lowered and removed. The open end of the tube L is then closed with the tightly fitting stopper P, through which passes a tube conveying pure dry carbon dioxide to expel the gas from the unmeasured portions of the apparatus. When this has been accomplished, one end of the combustion-tube (weighed) K containing copper oxide is attached at R, and to the other end the tubes T and S are fitted for collecting the water produced during the combustion. S is an empty tube which receives the greater part of the water; TT are tubes filled with calcium chloride. The stream of carbon dioxide is continued until all the air has been expelled from the combustion-tube and drying apparatus, and the whole apparatus is then left for at least an hour, so as to assume the temperature of the room. The height of the barometer, the temperature, and the level of the mercury at B and in the tube C are then noted, and from these data the volume of gas to be used for combustion, is calculated.

The combustion tube lying in a trough lined with magnesia is now heated to redness, the stopcock O is closed, G and N are opened, and mercury gradually allowed to flow into the reservoir E; by this means the gas in A is driven over the red-hot copper oxide. When the

mercury reaches H, the stopcock G is closed and O opened, and the carbon dioxide (which during the combustion has been escaping by the tube Q) now serves to expel the gas remaining between H and K. The lamps are now withdrawn, the stream of carbon dioxide continued till the tube is quite cold, when it is displaced by dry air. The combustion tube and the drying tubes are weighed before and after the combustion; and from the amount of water obtained the total hydrogen is calculated. The boron, of course, remains in the combustion tube, being chiefly deposited near R.

The capabilities of the apparatus were first tested by a series of combustions with pure hydrogen, and the results were sufficiently satisfactory to justify us in using the apparatus for the analysis of the hydride. The following results were obtained:—

(a.) *With pure Hydrogen.*

Experiment.	Corrected vol. of gas.	Loss in CuO tube.	Water found.	Water calculated.	Difference.
	c.c.	gram.	gram.	gram.	
I	665·29	0·4735	0·5345	0·5365	− 0·0020
II	657·97	0·4695	0·5280	0·5306	− 0·0026
III	673·62	0·48075	0·5435	0·5432	+ 0·0003
IV	658·22	0·46925	0·5290	0·5308	− 0·0018
V	660·69	0·4699	0·5327	0·5328	− 0·0001
VI	650·05	0·4637	0·5218	0·5242	− 0·0024

(b.) *With the Gas containing Boron Hydride.*

Experiment.	Corrected vol. of gas.	Loss in CuO tube.	Water found.	Calculated for pure H.	Difference.
	c.c.	gram.	gram.	gram.	
VII	668·80	0·4757	0·5424	0·5377	+ 0·0047
VIII	668·72	0·4778	0·5400	0·5392	+ 0·0008
IX	637·93	0·4572	0·5160	0·5144	+ 0·0016
X	653·91	0·4687	0·5290	0·5273	+ 0·0017

It will be seen at once from these results that the amount of water produced in the two sets of experiments does not differ much. Nevertheless, in the first series it is (with one exception) *less** than the calculated amount, whereas in the second series it is uniformly *greater*. This at least shows the exceedingly minute quantity of the hydride in the gas used for analysis, and it also indicates that the hydride must

* The deficiency is no doubt due to the occlusion of hydrogen by copper noticed by Graham, Lietzenmayer, Johnson, and other chemists.

contain *more* than 2 atoms of hydrogen in the molecule, for had it contained 1 or 2 atoms, then the quantity of water produced would have been respectively less than or the same as that obtained from hydrogen alone.

Although it is manifest that too much value must not be attached to the results of experiments which deal with such minute quantities, we have yet ventured to deduce from them a formula for the new compound. Taking the most successful experiment (No. 7), we see that 666·8 c.c. of the gas yielded 0·5424 gram of water; the same volume of pure hydrogen would have yielded 0·5377, the excess 0·0047 gram corresponds to 0·0005 gram hydrogen, which represents the quantity of that element in combination with boron over and above that required for the formula BH_2. Let us represent the formula as BH_{2+x}. In the same experiment the water obtained (0·5424 gram) corresponds to 0·4821 gram oxygen, exactly the amount which the copper oxide tube should have lost. It really did lose 0·4757 gram, the difference 0·0064 gram represents the boron retained with the copper oxide. The value of x is obviously obtained by the following proportion : $0{\cdot}0064 : 11 :: 0{\cdot}0005 : x = 0{\cdot}86$; hence 11 parts of boron are combined with 2·86 parts hydrogen, which may be considered, under the circumstances of the experiment, a sufficiently near approximation to BH_3.

Summary.

1. Magnesium boride is prepared—

   (*a.*) By heating magnesium with boric anhydride.

   (*b.*) By direct union of boron and magnesium.

   (*c.*) By the action of magnesium on boron trichloride.

2. Boron hydride is obtained from the magnesium boride on addition of an acid, but is mixed with a large excess of hydrogen.

3. The gas burns with a green flame, is decomposed by heat, with separation of boron; dissolves slightly in water, and gives a black precipitate with silver nitrate containing silver and boron.

4. It combines with ammonia, yielding a compound which is decomposed by acids.

5. The composition of the hydride, so far as could be ascertained by combustion of the gas with copper oxide, is represented by the formula BH_3.

XXXIII.—*On the Action of Benzoic Acid on Naphthaquinone.*

By Francis R. Japp, M.A., Ph.D., Demonstrator in the Chemical Research Laboratory, Science Schools, South Kensington, and N. H. J. Miller.

Preparation of Naphthaquinone.

The naphthaquinone employed in the following experiments was prepared by the method of Groves (*Chem. Soc. J.*, 1873, 209), by the oxidation of naphthalene with chromic anhydride in acetic acid solution. In order to get rid of unattacked naphthalene, Groves recommends that the mixture of naphthalene and naphthaquinone should be exposed to the air for some days in a warm place. This process is somewhat tedious; so, with a view to finding a shorter method, we made some experiments on the relative solubilities of naphthalene and naphthaquinone. We found that a hot mixture of equal volumes of glacial acetic acid and water dissolves naphthalene readily, but deposits very nearly the whole of the hydrocarbon on cooling to 20°; whereas of the naphthaquinone, which is dissolved under similar conditions, a considerable portion is retained in solution in the cold, and may be precipitated by diluting with an equal volume of water, and still more thoroughly by subsequent partial neutralisation with sodium carbonate. Following up this observation we endeavoured to employ in the separation of the naphthalene and naphthaquinone the acetic acid which serves as a solvent during the oxidation. This we have accomplished in the following process:—

Into each of ten flasks, 10 grams of naphthalene and 60 grams of glacial acetic acid are introduced. After heating to dissolve the naphthalene, a solution of 30 grams of chromic acid in 20 c.c. of water is gradually added to each flask. (A preliminary experiment showed that the presence of this proportion of water did not cause a precipitation of naphthalene from the hot solution.) In practice it is best to prepare this solution of chromic anhydride on a large scale, dividing it afterwards into portions of 50 grams each, by means of a measure constructed for this purpose. The chromic solution must be very gradually, taking the flasks in rotation: by hurrying the action the yield is much diminished. When the whole of the oxidising agent has been introduced, the contents of the flasks are united and heated over a water-bath to complete the reaction, after which 300 c.c. of water are added, a portion of this water being employed to rinse out

the small flasks.* The whole is then heated for a few minutes on the water-bath, agitating thoroughly, and is then allowed to cool. As soon as the temperature has sunk to about 20°, the liquid is filtered rapidly through calico. The filtration must not be postponed too long, as part of the naphthaquinone otherwise separates out. The filtrate is diluted with an equal volume of water, which occasions the separation of a great portion of the naphthaquinone, and is then partially neutralised with crystallised sodium carbonate. The naphthalene on the calico filter is again extracted with about 300 c.c. of a hot mixture of equal volumes of glacial acetic acid and water; the liquid is left to cool, filtered from the naphthalene, and treated as above. This second extraction is generally sufficient to exhaust the napthalene. The finely-divided napthaquinone is separated by filtration from the partially neutralised liquids, dried, and purified by crystallisation from light petroleum as recommended by Groves. In this way it is freed from a reddish-brown product, insoluble in petroleum. A petroleum of sp. gr. 0·72 was found very suitable.

The yield of pure naphthaquinone was 20 per cent. of the weight of naphthalene employed.

Action of Benzoic Acid on Naphthaquinone.

When naphthaquinone is heated with three times its weight of benzoic acid in a flask to about 160°, the liquefied mass speedily assumes a darker colour, at the same time almost solidifying from the separation of minute crystalline needles. Water is eliminated during the reaction, escaping in bursts of steam from the semi-solid mass and condensing in drops in the upper part of the flask. As soon as the quantity of crystalline substance no longer visibly increases, the reaction is stopped, and the contents of the flask, after cooling, are boiled with alcohol to dissolve the excess of benzoic acid, filtered, and washed with boiling alcohol on the filter. The crude substance, of which the yield is about equal to the weight of naphthaquinone employed, is thus obtained in small reddish-brown needles. It is insoluble in all the usual solvents, even at their boiling points; but aniline and bisulphide of carbon, when heated with it in sealed tubes to 300°, dissolve small quantities, the substance crystallising out in larger needles on the walls of the tube on cooling. Of course as a mode of purification, this last method is not applicable. We found, however, that the greater part of the colouring matter could be removed by

* 500 c.c. of water have thus been added to 600 grams of acetic acid. These proportions, which were found to work well in practice, were employed instead of equal volumes, in order to allow (roughly) for the formation of water during the oxidation and for the presence of a portion of the acetic acid as chromic acetate.

long-continued boiling with aniline. After treatment with aniline, the substance was again boiled with alcohol, and was thus ultimately obtained of a pale reddish-brown colour. Its weight was reduced by one-half in this process of purification. Under the microscope it now presented a perfectly homogeneous appearance, and consisted of fine ramiform needles. It is highly electric. It fuses above the range of the thermometer. Caustic alkalis do not dissolve it. We satisfied ourselves by means of a qualitative test for nitrogen, which gave a negative result, that the aniline employed in the purification had not combined in any way with the substance.

Analysis yielded the following results:—

	Substance.	CO_2.	OH_2.
I	0·1580	0·4876	0·0456
II	0·1392	0·4294	0·0386
III	0·1510	0·4666	0·0428

These numbers lead to the formula C_9H_4O—

	Calculated for C_9H_4O.		Found.			
			I.	II.	III.	Mean.
C_9 ..	108	84·37	84·16	84·13	84·27	84·18
H_4 ..	4	3·13	3·20	3·06	3·14	3·13
O ..	16	12·50	—	—	—	(12·69)
	128	100·00				100·00

Analyses I and II were made with one preparation of substance; in III a second preparation was employed.

By tripling the above empirical formula, so as to give the molecular formula $C_{27}H_{12}O_3$, the formation of this substance might be accounted for by the following equation:—

$$\underset{\text{Naphtha-quinone.}}{2C_{10}H_6O_2} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} = \underset{\text{New compound.}}{C_{27}H_{12}O_3} + 3OH_2.$$

To this higher molecular weight the physical properties of the substance also point. In view, however, of the difficulty of dealing with a substance which cannot be purified by recrystallisation, which does not possess a fusing point capable of being appealed to in the comparison of different preparations, and of which the only test of purity is the frequently fallacious one of apparent homogeneity under the microscope, we offer the above formula with all reserve. The study of the reactions of the substance, the details of which are given further on, has thrown but little light on its constitution.

An experiment was made to determine whether the compound could

be prepared by heating together benzoic anhydride and naphthaquinone at 160°; but, though the operation was continued for a long time, no trace of the compound was formed. The experiment was repeated, employing a higher temperature, but again with negative result. From this it would appear that the presence of the hydroxyl group in benzoic acid is necessary to the formation of the compound.

Oxidation.—In order to ascertain whether benzoic acid could be regenerated from the compound by oxidation, 1 gram was boiled with a mixture of potassic dichromate and dilute sulphuric acid. After boiling for about 18 hours, the substance had almost entirely disappeared. The liquid was then distilled with steam, and the distillate, after rendering alkaline, was evaporated to a small bulk and acidified with hydrochloric acid. No trace of benzoic acid could be detected.

In order to test for other acids, a second oxidation was performed with potassium permanganate in aqueous solution. 10 grams of the substance were treated in this way with 5 grams of permanganate. As soon as the permanganate was reduced, the solution was filtered from the mixture of manganic hydroxide and unattacked substance, the filtrate being preserved, and the precipitate subjected afresh to the oxidising action of 5 grams of permanganate. This was repeated several times, the solution being filtered after each operation, in order that any soluble products of oxidation might be withdrawn as quickly as possible from the further action of the permanganate. As soon as the reduction of the permanganate slackened, the process was finally interrupted, and the united filtrates, after evaporating to a small bulk, were acidified with hydrochloric acid and extracted with ether. About a gram of a solid crystalline acid was thus obtained, but, as it was of a yellowish colour, it was converted into a sodium salt and treated in aqueous solution with a very small quantity of permanganate on the water-bath. The resulting colourless solution yielded a perfectly white acid, readily soluble in hot water, and crystallising on cooling in small plates, fusing at 182°, which is the fusing point of phthalic acid. By sublimation, long characteristic needles of phthalic anhydride were obtained, fusing at 128·5—129·5°. We could not detect any other acid in the product of oxidation.

All other experiments yielded either negative results or such small quantities of product that examination was impossible.

Action of Hydriodic Acid and Amorphous Phosphorus.—After heating for four hours to 250°, the substance was recovered unaltered.

Distillation with Zinc-dust.—The substance was distilled from combustion-tubing with ten times its weight of zinc-dust. Two experiments were made, each with a gram of substance. In one the heating was carried backwards from the open towards the closed end of the

tube: in the other, forwards, beginning at the closed end. About one drop of an oily liquid, smelling like a high-boiling coal-tar oil, was obtained in each case.

Fusion with Potash.—No action took place till a temperature was reached at which the substance inflamed, and burnt like tinder on the surface of the potash. Even when previously mixed with potash and water, the substance behaved in exactly the same manner, separating out on the surface as soon as the water was driven off.

Distillation with Soda-lime.—The heating was carried forwards from the closed end of the tube. Nothing was obtained beyond a slight sublimate of unaltered substance.

Action of Zinc-ethyl.—Treated with zinc-ethyl at 100°, the substance does not evolve gas. It therefore contains no hydroxyl-group.*

Beyond showing that the compound contains the group $C_6H_4(C_2)^{vi}$ [1 : 2], and that it contains neither the group $C_6H_5—C\equiv$, nor hydroxyl, the above experiments are inconclusive. The absence of the group $C_6H_5—C\equiv$ shows that, assuming the substance to be formed in the manner expressed by the equation, the nucleus of the benzoic acid undergoes modification during the reaction, probably by the direct attachment of carbon of the naphthaquinone. The $C_6H_4(C_2)^{vi}$ group may belong either to a naphthaquinone residue, or—less probably, however—to a modified benzoic acid residue.

We propose provisionally to name the compound *benzonaphthone.*

The reaction is interesting as showing benzoic acid, a substance usually very inert in its behaviour towards neutral organic bodies, in a somewhat new light.

According to preliminary experiments which we have made, naphthaquinone also reacts with the following acids:—Of the formic series—formic, acetic, propionic, butyric, isobutyric, and stearic acids; of the benzoic series—phenylacetic acid—hydrocinnamic acid being, however, apparently without action; of the oxalic series—oxalic and succinic acids. It does not react with lactic acid. In many of these cases mixtures of compounds appear to be formed. We hope, however, to find among the products of these reactions substances somewhat

* In a paper by Japp and Wilcock, the non-evolution of gas when a substance is treated with *cold* zinc-ethyl is suggested as a general test for the absence of hydrogen directly attached to oxygen or nitrogen (*Chem. Soc. Trans.*, 1881, 665, foot note). I have since found that the test as thus employed frequently leads to erroneous results, inasmuch as, although substances containing the hydroxyl-group or the amido-group evolve gas under these conditions, those containing the imido-group generally require heating with the zinc-ethyl before any evolution of gas occurs. The substance ought to be added to the zinc-ethyl already heated to 100°. – F.R.J.

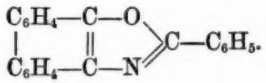
more amenable to ordinary chemical treatment than the compound here described.

Other quinones, so far as our observations have as yet extended, do not appear to react with acids.

XXXIV.—*On the Action of Aldehydes on Phenanthraquinone in Presence of Ammonia. (Second Notice.)*

By Francis R. Japp, M.A., Ph.D., Demonstrator in the Chemical Research Laboratory, Science Schools, South Kensington, and Edgar Wilcock.

In a previous communication (*Chem. Soc. J.*, Trans., 1880, 661) we described a compound obtained by the action of benzaldehyde containing hydrocyanic acid on phenanthraquinone. We named this compound *benzenylamidophenanthrole*, and assigned to it the constitution—



Just as we had almost completed the investigation, we found that this compound could be prepared more easily by heating together phenanthraquinone, benzaldehyde, and aqueous ammonia. In order that the reaction with hydrocyanic acid may take place, a temperature of 220—230° is required, and we were thus led to employ a similarly high temperature in working with ammonia. This is, as we have since found, quite unnecessary: the reaction is complete at 100°, and the operation may be conveniently conducted in an open flask on a water-bath.

Fifty grams of phenanthraquinone are introduced into a flask, and an excess of benzaldehyde (over 1 mol.) is added. After thoroughly mixing, strong aqueous ammonia is poured in, shaking the flask and stirring the contents with a rod. There ought to be sufficient ammonia to moisten the mass throughout, leaving an excess of the aqueous liquid. The flask is then heated on a water-bath, shaking from time to time. The pasty mass first liquefies, whilst bubbles of gaseous ammonia escape; after a short time it again becomes pasty, and finally solidifies. The reaction is generally complete in the course of a few minutes. The flask is then broken, the solid cake of substance is

powdered in a mortar with water, boiled, first with water and then with alcohol in order to remove any colouring-matter, and finally crystallised from hot benzene. After a couple of crystallisations, the substance is perfectly pure.

It crystallises, as described in our former paper, in large tufts of colourless silky needles, fusing at 202°. The yield is apparently almost theoretical.

We shall now proceed to describe some similar compounds obtained from phenanthraquinone and ammonia with other aldehydes.

Cumenylamidophenanthrole, $C_{14}H_8\langle{}^{O}_{N}\rangle C—C_6H_4—C_3H_7$.—This compound was prepared like the above, substituting cuminaldehyde for benzaldehyde. It was purified by crystallisation from a mixture of equal volumes of benzene and light petroleum, which at its boiling point readily dissolves the substance and deposits it in large tufts on cooling.

Properties.—Crystallises in tufts of colourless needles, with a silky lustre, and is in outward appearance indistinguishable from the benzaldehyde compound. Fuses at 186°. Sublimes slightly at a high temperature. Very soluble, even in the cold, in ether, bisulphide of carbon, chloroform, and benzene; also in boiling acetic acid, the solution solidifying to a mass of needles on cooling; slightly soluble in alcohol and light petroleum. Soluble in cold concentrated sulphuric acid, yielding a yellowish-green fluorescent liquid, which turns red on standing.

Analysis yielded the following results:—

I. 0·2650 gram gave 0·8319 gram carbonic anhydride and 0·1373 gram water.

II. 0·1628 gram gave 0·5110 gram carbonic anhydride and 0·0832 gram water.

III. 0·2201 gram, burnt *in vacuo* with copper oxide, gave 7·99 c.c. (calibrated vol.) nitrogen at 17° and under 738·3 mm. pressure, corresponding to 0·00918 gram nitrogen.

	Calculated for $C_{24}H_{19}NO$.		Found.			
			I.	II.	III.	Mean.
C_{24}..	288	85·46	85·61	85·61	—	85·61
H_{19}..	19	5·64	5·76	5·69	—	5·72
N...	14	4·15	—	—	4·17	4·17
O...	16	4·75	—	—	—	(4·50)
	337	100·00				100·00

The following equation expresses the mode of formation of this substance :—

$$\underset{\text{Phenanthra-quinone.}}{C_{14}H_8O_2} + \underset{\text{Cuminaldehyde.}}{C_{10}H_{12}O} + NH_3 = \underset{\text{Cumenylamido-phenanthrole.}}{C_{24}H_{19}NO} + 2OH_2.$$

Furfurenylamidophenanthrole, $C_{14}H_8\begin{smallmatrix}O\\ \diagup\\ N\end{smallmatrix}\!\!>\!C—C_4H_3O$.—This substance was obtained from furfuraldehyde, phenanthraquinone, and ammonia. The yield was not quite so good as in the former cases, dark-coloured products being formed at the same time, the presence of which interfered with the process of purification. By boiling its solution in amyl alcohol with animal charcoal for some hours, and recrystallising two or three times from this solvent, the substance was obtained perfectly pure.

Properties.—Crystallises in tufts of colourless silky needles; sometimes, however, when deposited quickly from a hot acetic acid solution, in shining leaflets. Fuses at 231°. Sublimes more readily than the cuminaldehyde compound. Readily soluble in boiling amyl alcohol, in glacial acetic acid, and in benzene; only slightly soluble in these liquids in the cold; moderately soluble in chloroform, less so in bisulphide of carbon; very slightly soluble in ether and in light petroleum; almost insoluble in alcohol. Dissolves in cold concentrated sulphuric acid, yielding a reddish-brown liquid with a blue fluorescence.

The results of analysis agreed well with the theory :—

I. 0·1807 gram gave 0·5285 gram carbonic anhydride and 0·0623 gram water.

II. 0·1759 gram gave 0·5143 gram carbonic anhydride and 0·0627 gram water.

III. 0·0615 gram, burnt *in vacuo* with copper oxide, gave 2·9 c.c. (calibrated vol.) nitrogen at 17·3° under 675·8 mm. pressure, corresponding to 0·00304 gram nitrogen.

	Calculated for $C_{19}H_{11}NO_2$.		Found.			
			I.	II.	III.	Mean.
C_{19} ..	228	80·00	79·76	79·74	—	79·75
H_{11} ..	11	3·86	3·83	3·96	—	3·89
N ..	14	4·91	—	—	4·94	4·94
O_2 ..	32	11·23	—	—	—	(11·42)
	285	100·00				100·00

Action of Acetaldehyde on Phenanthraquinone in presence of Ammonia.

By means of this reaction we had hoped to obtain *ethenylamidophenanthrole*, but the result did not correspond with our expectation. When aqueous ammonia is employed, and the process is conducted as in the case of the benzaldehyde compound, no reaction takes place beyond a partial reduction of the phenanthraquinone. If, however, phenanthraquinone is heated with aldehyde-ammonia, the substances act on each other with elimination of water. The product of the reaction was a dark-coloured resinous mass, from which dilute hydrochloric acid extracted a basic substance. The base, precipitated by an alkali, formed a brown jelly which turned pale-yellow on exposure to the air. It was not volatile without decomposition. It very closely resembled in its properties some of the amorphous basic substances obtained from aldehyde-ammonia alone; we convinced ourselves, however, by an oxidation experiment, in which phenanthraquinone was formed, that a phenanthrene derivative was present. All the salts which we examined were amorphous, and as we could find no means of purifying the substance, we abandoned its investigation.

We have partially investigated the action of a hydroxyaldehyde—salicylaldehyde—on phenanthraquinone in presence of ammonia, and have found that the reaction takes place according to the equation—

$$\underset{\text{Phenanthra-quinone.}}{C_{14}H_8O_2} + \underset{\text{Salicyl-aldehyde.}}{C_7H_6O_2} + 2NH_3 = \underset{\text{New com-pound.}}{C_{21}H_{14}N_2O} + 3OH_2.$$

The compound thus formed contains two atoms of nitrogen in the molecule, instead of one, as in the case of the compounds already described. This investigation will be continued by one of us with a view towards ascertaining the constitution of this compound. A study of the same reaction with parahydroxybenzaldehyde will probably show whether the above abnormal result is due merely to the presence of a hydroxyl-group, or to the position of that hydroxyl-group in the molecule.

XXXV.—*Note on the Appearance of Nitrous Acid during the Evaporation of Water.*

By Robert Warington.

The statements of Schönbein that whenever pure water or an alkaline solution is evaporated nitrite of ammonium is produced, and that the same salt is also formed during ordinary combustion in the air,* have led to many investigations and to much difference of opinion. It is probably now acknowledged by most chemists, although contrary statements are still to be found in text-books, that nitrous acid and ammonia are not, as Schönbein supposed, produced from the elements of air and water in either of these operations, but that their occurrence is due to impurities in the materials employed, or in the atmosphere in which the experiment is conducted. The experiments of L. V. Wright (*Trans. Chem. Soc.*, 1879, 42) may be quoted as showing that the nitrous acid formed during the combustion of coal gas and hydrogen in air is really due to the oxidation of ammonia present either in the gas or in the surrounding atmosphere. The experiments of Carius (*Ann. Chem.*, 1874, **174**, 32), in which pure water was evaporated at various temperatures in a stream of pure air, without either nitrous acid or ammonia being found in the distillate or residue, prove equally that the production of these bodies is not at least a necessary accompaniment of evaporation. The facts observed by Schönbein remain, however, substantially true, notwithstanding that our interpretation of them may differ from his. It is undeniable that pure water, if evaporated to a small bulk by ordinary means, will generally be found to contain nitrous acid. To point out some of the conditions which determine this occurrence is the object of the present communication.

Attention was first drawn to the subject by observing that a sample of rain-water, which gave no reaction with metaphenylenediamine, gave, after concentration to a quarter of its volume, so well-marked a reaction with this test, that there was little room for doubt that nitrous acid had been acquired during evaporation. An experiment made with distilled water confirmed this idea. One litre of distilled water with 5 c.c. of lime-water, evaporated to a small bulk over a Bunsen burner, gave an abundant reaction for nitrous acid with the metaphenylenediamine. It was now obvious that the subject required some attention, as it would be impossible to determine with exactness

* A full account of Schönbein's experiments will be found in the *Chemical News*, 1862, **6**, 241.

the nitrates present in rain, or in any other highly dilute solution, if nitrous acid were acquired during the process of concentration.

Experiments were next made on the evaporation of distilled water by various means, water from the same bulk being used in all the trials. This water gave no reaction with the metaphenylenediamine test, nor with the still more delicate naphthylamine test, which we shall speak of more fully further on.

One litre of this water, with 5 c.c. of pure lime-water, was first distilled in a retort connected by an air-tight joint with a receiver, the whole apparatus being nearly exhausted of air by means of a water-pump before distillation commenced. Distillation was carried on till only about 20 c.c. of water remained in the retort. This concentrated residue, tested with metaphenylenediamine, gave no reaction of nitrous acid.

The same experiment was again repeated, this time with the retort and receiver full of air. The concentrated water was again found to contain no nitrous acid.

It was evident from these two experiments that the source of nitrous acid was to be found in the air, and that protection from the atmosphere was a sufficient safeguard against its appearance in water during its evaporation.

The original mode of evaporation was next repeated in a quantitative manner. One litre of distilled water, with 5 c.c. of lime-water, was concentrated in a glass basin $6\frac{1}{4}$ inches in diameter over a Bunsen gas burner having a rose jet. The evaporation was conducted in a quiet room in which no other work was in progress. In four hours the bulk of water was reduced to 20 c.c. This residue gave a strong reaction with metaphenylenediamine. By comparing the tint with that given by a standard solution of nitrite, it appeared that about 0·05 milligram of nitrogen, in the form of nitrous acid, was present.

It seemed very probable that the greater part of this nitrous acid had arisen from the combustion of the coal gas used as fuel, nitrous acid being known to be formed during such combustion, and the basin containing the water being necessarily enveloped in the gaseous products from the flame. Several experiments were therefore made in which the same bulk of water was evaporated in the same basin and in the same room, but without the use of gas.

An experiment with alcohol as fuel was not very successful; the source of heat being feeble the evaporation took a long time, and the water was consequently much exposed to air. The nitrous acid found was considerable, though distinctly smaller than that arising during the short evaporation over gas.

The use of steam proved far more successful. The steam was generated by boiling water containing caustic potash. The steam was

led into the room from a closed cupboard, such as is generally found in laboratories, the products of combustion of the fuel used to boil the water being conveyed off by the flue attached to the cupboard and thus not entering the room. No gas was burnt in the room during the experiment. Under these conditions a litre of distilled water, with 5 c.c. of lime-water, was evaporated in the glass basin in five hours to 20 c.c. The residue contained a far smaller quantity of nitrous acid than in any previous instance of evaporation in an open basin; the nitrogen as nitrous acid amounted to about 0·004 milligram, or about $\frac{1}{12}$th the quantity found after evaporation over gas.

It was thus proved that the greater part of the nitrous acid previously found had been acquired from the products of combustion of the fuel employed to effect the evaporation; a small part of the nitrous acid was apparently, however, due to mere exposure to the air of the room. That this was really the case was shown by a check experiment carried out at the same time as the evaporation over steam last named.

By the side of the steam-bath was placed a basin of distilled water, similar in all respects to that undergoing evaporation; portions of this water were tested from time to time by the delicate naphthylamine test. After two hours' exposure to air a minute trace of nitrous acid was recognised in the water; after five hours this had become quite distinct; at the end of 24 hours a full rose-tint was developed. The distilled water had thus gradually acquired nitrous acid from the air of the room without any sensible amount of evaporation having taken place.

The result of these few experiments is to show that the only perfectly safe mode of concentrating a water is by distillation in a closed vessel, but that fair results may be obtained by evaporation over steam. The danger of the acquisition of nitrous acid during evaporation in an open vessel is diminished in proportion to the purity of the surrounding atmosphere, and to the rapidity with which the evaporation is conducted. Gas is clearly an extremely objectionable fuel to employ in such evaporations.*

I will now add a few words on the subject of the extremely delicate naphthylamine test for nitrous acid, which enables us to detect the presence of nitrous acid in the atmosphere. This test is described by Griess (*Ber.*, 1879, 427), and is stated by him to be far more delicate than the reaction with metaphenylenediamine which he had previously recommended. My attention was called to this test by Dr. O. N. Witt, who also most kindly placed at my disposal the reagents required for its performance.

* I have already pointed out (*Journ. Chem. Soc.*, 1873, 986) that the evaporation of water over London gas results in the acquisition of sulphuric acid by the water.

Griess directs that the solution to be tested shall be slightly acidified with sulphuric acid, a few drops of an aqueous solution of sulphanilic acid are next added, and after waiting 10 minutes, a few drops of an aqueous solution of sulphate of naphthylamine. Nitrous acid, if present, forms, with the sulphanilic acid, a diazo-compound, which is further converted by the naphthylamine into a body having a beautiful rose colour. In extremely weak solutions the tint may take an hour or more to develop; in strong solutions a dark precipitate speedily separates. The test is most suitable as a reaction for very small quantities of nitrite.

In employing this test I have used exclusively hydrochloric acid and hydrochloride of naphthylamine. It is apparently unnecessary to wait between the addition of the two reagents, as recommended by Griess, equally good results being obtained by adding them simultaneously. Experiments made with a standard solution of nitrite of potassium, prepared from pure nitrite of silver, and diluted to various degrees with distilled water giving no reaction with the test, have yielded the following results. The experiments were made in test-tubes, the columns of liquid being about three inches deep. To 10 c.c. of the solution to be tested were added successively one drop of dilute hydrochloric acid (1 : 4), one drop of a nearly saturated solution of sulphanilic acid, and one drop of a saturate solution of hydrochloride of naphthylamine.

With a solution containing 1 part of nitrogen as nitrous acid in 1,000,000 parts of water, an immediate pink colour was produced, which rapidly increased in intensity, and finally became a deep ruby red.

With a solution containing 1 part of nitrogen as nitrous acid in 10,000,000 parts of water, there was an almost immediate development of a pink tinge, which at the end of an hour had deepened into a full rose colour.

With a solution containing 1 part of nitrogen as nitrous acid in 100,000,000 parts of water, a pink tinge first became perceptible at the end of six minutes; at the end of an hour the solution was of a distinct pale pink colour.

An experiment was made with a solution containing 1 part of nitrogen as nitrous acid in 500,000,000 parts of water. 1 c.c. of a solution of nitrite, containing one per million of nitrogen, was placed in a half-litre flask, which was then filled to the mark with distilled water, and five drops of each of the three reagents were added, the whole being well mixed and the flask stoppered. By the side of this was placed another half-litre flask containing nothing but distilled water, and the same quantity of reagents that had been added to the first flask. A pink tinge began to appear in the first flask before two hours had expired, and gradually became more distinct. At the end of 24

hours a three-inch column of the fluid viewed in a test-tube had a faint but distinct pink tinge, the colour of the mass of liquid in the flask was of course more marked. No pink colour whatever appeared in the flask to which no nitrite had been added.

An exactly similar experiment was next conducted in two litre flasks, the dilution being now 1 part of nitrogen as nitrous acid in 1,000,000,000 parts of water, and 10 drops of each reagent being employed. The development of colour in this case was rather slower, but an alteration in tint was visible in two hours. At the end of 24 hours the mass of liquid in the flask had a distinct pink tinge, but a three-inch column in a test-tube could not be certainly pronounced as pink without comparison with a similar test-tube filled only with distilled water. The distilled water in the duplicate flask developed no colour.

The metaphenylenediamine test tried with the same nitrite solutions gave only a faint reaction with that containing 1 part of nitrogen in 10,000,000, and no reaction at all when the dilution reached 1 part of nitrogen in 100,000,000.

The amount of delicacy possessed by the naphthylamine reaction is truly astonishing, and places it in the front rank of all qualitative tests. We have already seen that by its means it was possible to detect the presence of nitrous acid in the air. Freshly-prepared distilled water contains apparently no trace of nitrous acid, but in water exposed in a basin or wide beaker for two or three hours to the air of the laboratory a trace of nitrous acid can be detected. The amount of nitrous acid gradually increases with the length of exposure, and in 24 hours is sufficient to yield a full rose colour with the naphthylamine test. Distilled water supplied with the necessary reagents at starting, and placed in an open vessel, can be observed deepening in tint from day to day as the absorption of nitrous acid proceeds. The same mixture of water and reagents remains perfectly colourless when left in a half-filled stoppered bottle.*

Distilled water placed in a basin outside the laboratory was also found to acquire nitrous acid, but much more slowly.

An attempt was made to ascertain the presence of nitrous acid in the air of one of the fields on the Rothamsted Farm; the experi-

* The presence of nitrous acid in the air of the meeting room of the Chemical Society was shown at the reading of this paper. Two cylinders each containing about 200 c.c. were nearly filled with distilled water, to which a few drops of sulphuric acid, sulphanilic acid, and hydrochloride of naphthylamine had been added; one of these cylinders was covered with a watch-glass, and the contents of the other were emptied into a basin. After four hours' exposure to the air, the contents of the basin were returned to the empty cylinder. It was seen that the contents of the first cylinder had remained colourless, while the solution freely exposed to air had become rose-pink. The amount of nitrous acid in the atmosphere was apparently greater than that occurring in the air of the Rothamsted Laboratory.

ments were made during August and September, 1880. Considerable difficulty was met with from the access of insects to the basins. Three basins were finally started, two covered with fine copper gauze, the third with two thicknesses of filter-paper; each basin contained about half an inch of water; the basins were protected from rain, but freely exposed to air. In three days a trace of nitrous acid was perceptible in the water of both the gauze-covered basins, but none in that protected by filter-paper. In six days nitrous acid became perceptible in the water of the paper-covered basins and had increased in the others. The amount of nitrous acid continued to increase from day to day, and at the end of 27 days was estimated as amounting to 1 part of nitrogen in 15,000,000 of the remaining water in the gauze-covered basins; the water protected with filter-paper contained decidedly less. The air of the open country was thus, as might be expected, far purer than the air of the laboratory.

As nitrous acid is present in the air, it is of course of constant occurrence in rain. The rain-water collected at Rothamsted only occasionally contains sufficient nitrous acid to give a reaction with the metaphenylenediamine test, but it is only in exceptionally heavy rains that the nitrites become too diluted to affect the naphthylamine test.

XXXVI.—*Note on Usnic Acid and some Products of its Decomposition.*

By the late J. Stenhouse, F.R.S., and Charles E. Groves.

Usnic Acid.

The best method of obtaining pure usnic acid from the crude acid extracted from *Usnea barbata* by treatment with lime and water (*Chem. Soc. J.*, 1880, Trans., 236), is first to convert it into an insoluble basic compound, as formerly stated (*Proc. Roy. Soc.*, **18**, 223; also *Chem. Soc. J.*, *loc. cit.*). This compound, after being washed with hot water, is decomposed by boiling it with dilute hydrochloric acid in slight excess, collected, and well washed. The moist yellowish-brown product is then stirred up in cold water (about 10 parts to 1 of usnic acid); the usnic acid dissolved by adding soda solution in considerable excess; and the dark brown liquid filtered by means of a vacuum filter to separate the small quantity of insoluble mucilaginous matter, &c. As this impurity renders the filtration somewhat difficult, it is necessary to use excess of soda, for sodium usnate, although readily soluble in the alkaline solution, is not very soluble in cold water. As it was found that repeated crystallisation of the sodium compound of usnic acid—formerly

recommended as the best method of purification (*loc. cit.*)—caused considerable loss, owing to the decomposition which it undergoes when the solution is heated, advantage was taken of the comparative insolubility of the sodium compound in cold solution of sodium carbonate. For this purpose the impure dark-coloured solution abovementioned, containing sodium usnate together with excess of soda was treated with hydrogen-sodium carbonate in excess On adding this salt in fine powder to the solution, it dissolves, and when the quantity is sufficient to neutralise the free soda, a crystalline precipitate of nearly pure sodium usnate is produced; if excess of hydrogen-sodium carbonate has been employed, only traces of usnic acid remain in solution. The crystalline precipitate is collected, and after being washed with a little saturated solution of sodium carbonate (sp. gr. 1·14), it is again stirred up with distilled water, dissolved by means of soda solution in slight excess, and precipitated a second time by addition of hydrogen-sodium carbonate. On strongly acidulating the mother-liquors obtained in these operations, a small quantity of very impure usnic acid may be recovered. The sodium salt purified in the above manner is then dissolved in hot spirit by means of soda, and the solution strongly acidified with acetic or hydrochloric acid, which throws down usnic acid in the crystalline state. When cold it is collected, washed with spirit, or—if hydrochloric acid has been used—with water, and dried. In order to separate the minute quantity of mucilaginous matter which adheres very strongly to the acid and cannot be removed, even by repeated crystallisation from spirit, it must be crystallised from benzene. For this purpose, it is dissolved in 50 parts of hot benzene, filtered, and the solution concentrated by distillation, until its bulk is reduced to about one-half. On cooling, the pure usnic acid is deposited in brilliant yellow needles.

When pure sodium usnate is boiled with a dilute solution of hydrogen-sodium carbonate for several hours, care being taken to completely exclude the air, it is decomposed, giving a yellow solution, which turns black almost immediately on exposure to the air. If the yellow solution is carefully neutralised with dilute sulphuric acid, a brownish-yellow flocculent precipitate is obtained; this may be crystallised from spirit, in which it is very soluble. It is, perhaps, identical with the compound obtained by Paternò (*Gazz. chim. ital.*, **6**, 113), by the limited action of potash on usnic acid in an atmosphere of hydrogen.

Usnolic Acid.

Usnic acid dissolves very readily in concentrated sulphuric acid with development of heat, forming a deep orange-brown coloured solution, from which water precipitates the usnic acid almost entirely unaltered.

If, however, the solution be heated, it becomes darker, and eventually blackens, and gives off sulphurous anhydride. By carefully regulating the temperature, this may be avoided, and then the usnic acid is converted into a new compound, which is thrown down as a curdy precipitate on pouring the acid solution into water. The following is the best method of proceeding:—1 part of pure usnic acid is dissolved in 3 parts by weight of cold concentrated sulphuric acid, the solution being facilitated by stirring the mixture, which gradually becomes warm. As soon as all the crystals have disappeared, the deep orange-coloured solution is heated for three hours at 60°; when cold, the viscid liquid product is poured into 15 parts water, the flocculent precipitate is collected, washed by stirring it up with 30 parts of cold water, and after standing some time, it is again collected on a vacuum filter. As the precipitate, from its porous nature, retains sulphuric acid with great obstinacy, it cannot be dried, even at a gentle heat, without decomposition; so that to remove the water it is necessary to boil it with spirit (10 parts) for a short time. This does not dissolve the whole of the substance, but serves to remove all the water and any sulphuric acid that may be present. After standing for 24 hours, the crystalline product is collected, dissolved in 40 parts of boiling spirit, and the filtered solution distilled down to one-half. On standing, the usnolic acid separates in small crystals.

Pure usnolic acid forms small, yellowish prisms (m. p. 213·5°), which are almost insoluble in benzene, carbon bisulphide, or ether, and only sparingly soluble in boiling spirit, a comparatively small portion crystallising out as the solution cools. It dissolves readily in dilute alkaline solutions with an orange-brown colour, and the addition of an acid causes unaltered usnolic acid to be precipitated in yellowish flocks. Dried at 100° and burnt in a current of oxygen, it gave the following results:—

I. 0·1755 gram substance gave 0·411 gram carbonic anhydride, and 0·080 gram water.

II. 0·178 gram substance gave 0·416 gram carbonic anhydride, and 0·083 gram water.

III. 0·176 gram substance gave 0·412 gram carbonic anhydride, and 0·077 gram water.

IV. 0·218 gram substance gave 0·509 gram carbonic anhydride, and 0·098 gram water.

			I.	II.	III.	IV.	Mean.
C_{27} =	324	63·78	63·87	63·74	63·84	63·68	63·78
H_{24} =	24	4·72	5·06	5·18	4·86	4·99	5·02
O_{10} =	160	31·50	—	—	—	—	—
	508	100 00					

The analyses I and II were made from substance prepared by heating the mixture of usnic acid and sulphuric acid, at 50°; the unaltered usnic acid, which at this temperature always occurs along with the usnolic acid, being removed from the partially purified product by treatment with hot benzene, in which the usnolic acid is almost insoluble. A temperature of 60° was employed in the preparation of III and IV.

It is difficult at first to see what connection there is between the formula usually ascribed to usnic acid, $C_{18}H_{16}O_7$, and that of usnolic acid, $C_{27}H_{24}O_{10}$. It must be remembered, however, that the amount of hydrogen found by the different chemists who have analysed the former, has always been somewhat *less* than that required by the formula given; thus Stenhouse, as a mean of two analyses of usnic acid, found C = 62·66, H = 5·06; whilst Hesse found C = 62·80, H = 5·00. If we adopt for usnic acid the formula $C_{54}H_{50}O_{21}$, which requires C = 62·67, and H = 4·84, this anomaly with regard to the hydrogen disappears, and the carbon, as found by Hesse and by Stenhouse, agrees much more closely with the theoretical amount than it does with that required by the formula $C_{18}H_{16}O_7$. Moreover, if we double the formula of usnolic acid, and make it $C_{54}H_{48}O_{20}$, the relation between usnic acid and usnolic acid becomes evident, the usnic acid losing the elements of water under the dehydrating influence of the sulphuric acid.

Attempts were made to fix the molecular weight of usnolic acid, but without success. A solution of the neutral sodium salt yields a flocculent yellow precipitate of silver usnolate, when silver nitrate is added; but it rapidly acquires a darker colour when collected and washed, and becomes almost black on drying. Attempts to obtain an ethylic derivative by the action of ethyl iodide on the dried silver compound, yielded most unsatisfactory results.

XXXVII.—*Note on the Sweet Principle of* Smilax Glycyphylla.

By C. R. Alder Wright, D.Sc. (Lond.), Lecturer on Chemistry, and E. H. Rennie, B.Sc. (Lond.), M.A. (Sydney), Demonstrator in Chemistry in St. Mary's Hospital Medical School.

Substances have been described under the names of *parillin*, *smilacin*, and *sarsaparillin*, by Poggiale (*Ann. Chem. Pharm.*, **13**, 84), Thubeuf

(*ibid.*, **14**, 76), Petersen (*ibid.*, **15**, 74; and **17**, 166), and Flückiger (*Jahresbericht*, 1877, 906), obtained from ordinary medicinal sarsaparilla roots (*Smilax officinalis*) by making an alcoholic extract and concentrating it, when a crystalline body separates, to which the above-named authors have ascribed the formulæ $C_8H_{15}O_3$, $C_{15}H_{26}O_5$, and $C_{40}H_{70}O_{18}$, as representing their probable composition.

The leaves of the *Smilax glycyphylla* have long been used by herbalists and others in Australia as a remedy for scurvy and allied diseases, but no investigation of the sweet principle contained in them appears to be extant. The following preliminary note on the subject, therefore, may be of interest, although incomplete through want of material. It is proposed by the latter of us to complete the examination as soon as an opportunity presents itself of obtaining more material.

A concentrated aqueous decoction from about 20 lbs. of leaves and stems was prepared in Australia and sent to us: agitation with ether removed a substance readily crystallisable, and possessing the peculiar sweet taste of the extract. In order to prevent frothing on treatment with ether, albuminous substances, &c., were precipitated by addition of an equal bulk of alcohol, which was then distilled off after filtration: the residue, after two or three treatments with about its own bulk of ether, practically yielded nothing more to ether: on distilling off the ether and leaving the residue at rest, it became a yellowish crystalline mass readily soluble in boiling water, from which crystals (A) deposited: another sample of crystals (B) being obtained by spontaneous evaporation of the ethereal solution of a portion of (A) in contact with a little water. The mother-liquors of (B) deposited another crop of crystals (C) on further evaporation, whilst on recrystallising the remainder of (A) from water, crystals (D) were obtained. These four specimens on combustion gave the following numbers, after previous drying at 100°:—

	Carbon.	Hydrogen.	Previous loss at 100°.
Specimen A.....	60·00	5·82	16·47
„ B.....	58·89	5·69	11·40
„ C.....	59·75	5·91	11·49
„ D.....	58·68	5·73	16·66

On further examination all these specimens were found to retain a small quantity of substance precipitable by lead acetate. Specimen C and the residue obtained from the mother-liquors of A, B, C, and D by extraction with ether were accordingly dissolved separately in water, and treated with lead acetate, and then, after filtration, extracted with ether. The two sets of crystals thus obtained, E and F, were burnt and gave the following numbers:—

	Carbon.	Hydrogen.
Specimen E.....	58·16	5·52
„ F.....	58·00	5·52

The formula, $C_{13}H_{14}O_6$, requires carbon 58·65, hydrogen 5·26, whilst $C_{13}H_{14}O_6,2H_2O$ represents 11·59, and $C_{13}H_{14}O_6,3H_2O$ 16·88 per cent. of water of crystallisation.

It was not found practicable to obtain any compound or derivative of this substance, by means of which its molecular weight could be fixed.

On fusion with potash at 250°, acidifying the "melt," and extracting with ether, a crystallisable acid was obtained sparingly soluble in cold water, readily soluble in alcohol and ether. The alcoholic solution was decolorised by animal charcoal, and the acid crystallised from hot water. It then melted at 127—128°. In order to see whether it was homogeneous, it was again crystallised from hot water, and the melting point again determined, and found to be 127°. On combustion the following numbers were obtained:—Carbon, 64·97 per cent.; hydrogen, 6·37 per cent. These percentages agree very well with those required for $C_9H_{10}O_3$, viz., carbon, 65·06 per cent.; hydrogen, 6·02 per cent. A silver salt was then made by boiling the aqueous solution of the acid with silver carbonate and filtering the hot solution. On cooling the salt crystallised out. The silver was determined after separating, washing, and drying the crystals at 100°. The analysis yielded 39·50 per cent. of silver, $C_9H_9O_3Ag$ requiring 39·56 per cent.

On heating with soda-lime the acid gave off an odour and vapour resembling that of a phenol. When pure it gives no colour-reaction with ferric chloride. The above-described properties do not agree, so far as we have been able to ascertain, with those of any hitherto described acid. It probably has one of the formulæ

$$C_6H_2(CH_3)_2{<}\begin{matrix}OH\\COOH\end{matrix}, \quad \text{or} \quad C_6H_3.C_2H_5{<}\begin{matrix}OH\\COOH\end{matrix},$$

but the quantity at our disposal was too small to determine its constitution.

The original substance, when heated in a sealed tube with dilute hydrochloric acid, yielded a small quantity of an acid melting at 127°, and to all appearance identical with that produced by fusion with potash. The sweet principle is strongly attacked by nitric acid, yielding a clear yellow solution apparently containing oxalic and picric acids. Until further experiments, confirmatory of these results and serving to elucidate the composition of this sweet principle have been completed, it is hardly worth while to assign a name to it: apparently, however,

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it is dissimilar from the active principle of ordinary sarsaparilla (it appears to contain much less hydrogen) and from glycyrrhizin, which it somewhat resembles in taste: so that were its identity and distinctiveness established, the term *glycyphyllin* might perhaps be applied to it.

XXXVIII.—CONTRIBUTIONS FROM THE LABORATORY OF THE ROYAL COLLEGE OF CHEMISTRY, SCIENCE SCHOOLS, SOUTH KENSINGTON.

On New Zealand Kauri Gum.

By Edward H. Rennie, M.A. (Sydney), B.Sc. (Lond.).

This resin, which is the product of a coniferous tree (*Dammara Australis*) growing in New Zealand, seems to have been first examined in 1843 by R. D. Thomson (*Ann. Chim. Phys.* [3], **9**, 499), who obtained from it by distillation at a gentle heat an amber-coloured oil containing 82·2 per cent. carbon and 11·1 per cent. hydrogen, to which he gave the name *dammarol*.

It was again examined in 1874 by M. M. P. Muir (this Journal, 1874, 733), who obtained from it, by dry distillation, an oil boiling between 155° and 156° which contained 79·07 per cent. carbon and 10·90 per cent. hydrogen, to which he ascribed provisionally the formula $C_{10}H_{20}O_7$, stating, however, that the quantity at his disposal was too small to make certain of the purity of his product. Having a considerable quantity of the Kauri gum at my disposal, I have thought it worth while to re-examine it, especially with regard to the volatile oil above mentioned.

The resin exhibited physical properties very similar to those described by previous observers. It was thought better, instead of subjecting it to dry distillation, to place it in a copper vessel which was heated by a gas flame, and through which a rapid current of steam was kept passing. The distillation was continued until a semi-solid sticky product began to form in the condenser. In this way 15 lbs. of the resin yielded about 750 c.c. of oil. The latter having been separated from the water was fractionally distilled. A very small quantity came over below 156°, the greater part coming over between this temperature and 160°. A small quantity came over between 160° and 180°, but above this latter temperature scarcely anything

more could be got to distil over, even in a vacuum; the residue when cold being a sticky gelatinous mass. On repeated fractionation, nearly the whole of the oil came over between 157—159°, very small quantities being obtained from 160—170° and 170—180°. The portion from 157—159° was distilled three times over sodium (which acted very slightly upon it), and was then found to boil almost constantly between 157—158°. This final product had a strong odour of turpentine, and was perfectly colourless.

On combustion it yielded the following numbers:—

I. 0·2358 gram substance gave 0·2545 H_2O.
0·7600 CO_2.
II. 0·1290 gram substance gave 0·1428 H_2O.
0·4180 CO_2.
III. 0·2160 gram substance gave 0·2322 H_2O.
0·6954 CO_2.
IV. 0·1970 gram substance gave 0·2126 H_2O.
0·6344 CO_2.

These correspond with the following percentages:—

	I.	II.	III.	IV.	Required for $C_{10}H_{16}$.
Carbon	87·91	88·37	87·80	87·82	88·23
Hydrogen	11·99	11·29	11·94	11·99	11·77

The liquid had a specific gravity of 0·863 at 18°, and in a column of 300 mm. in length acted very slightly on polarised light, giving a rotation to the left of three to four degrees.

By the action of phosphorus pentasulphide for 7—8 hours it was for the most part resinised, but a small quantity of liquid distilled over below 190°. This by repeated distillation over sodium, treatment with strong sulphuric acid, and fractionation, yielded a liquid boiling at 174—178°, which had the odour, external characteristics, and composition of cymene, and on oxidation with chromic liquor yielded terephthalic and acetic acids.

Attempts were made to isolate some other substances from the higher-boiling portions of the original oil, but on fractionation they all tended to a higher and lower limit, the latter being about 160° and the higher above 200°, and, as already stated, the portions above 200° seemed to polymerise and form only a sticky mass which would not distil even *in vacuo*.

From the above facts, it appears that the oil produced in the distillation of Kauri gum consists almost entirely of a terpene boiling at 157—158°, and closely resembling the other members of the same family in its physical and chemical characteristics; the higher boiling portions of the original oil being apparently formed by polymerisation.

XXXIX.—*On the Action of Alcohol on Mercuric Nitrate.*

By Richard Cowper, F.C.S., Assoc. R.S.M., Demonstrator of Chemistry, Royal Naval College.

With the intention of preparing fulminate of mercury, some mercury had been dissolved in nitric acid, and, owing to circumstances, this solution was left standing for several days. Alcohol was then added, and the mixture heated, whereupon a precipitate formed, which was not fulminate of mercury. At the suggestion of Dr. Debus I undertook an investigation of this substance.

It appears that the formation of such a substance was first observed by Sobrero and Selmi (*Liebig's Annalen*, 1851), and shortly afterwards investigated by Gerhardt (*ibid.*), who describes it as consisting of a nitrate of ethyl the hydrogen of which is entirely replaced by mercury, crystallised with a molecule of mercuric nitrate and 2 mols. of water, and having the formula $C_4Hg_5(NO_3)_2.Hg(NO_3)_2 2OH_2$, agreeing closely with the numbers which he obtained by analysis. No difficulty was experienced in preparing the substance. Mercury is dissolved in twelve times its weight of nitric acid of sp. gr. 1·30. The solution is left at rest for several days until all nitrous fumes have escaped, and the liquid, which is blue at first, has become colourless. 12 parts by weight of pure alcohol of sp. gr. ·80 are then added, and the mixture is heated until the precipitate begins to form. The heat is then removed, and the substance continues to deposit for some hours. The crystalline precipitate so obtained is washed with alcohol and then with water, collected on a filter-paper, and dried over sulphuric acid.

Several quantities of the substance were prepared in this manner, the precipitate being withdrawn from the liquid at intervals as it formed. The different portions were kept apart and analysed.

The results obtained varied considerably—

H	from	0·30	to	0·41
C	„	3·03	„	3·52
Hg	„	76·0	„	81·3
N	„	2·4	„	3·6

and it became necessary to obtain some means of recrystalling the substance. It is quite insoluble in water, alcohol, or ether. Hydrochloric acid dissolves it with the greatest facility, but at the same time decomposes it, a peculiar, not unpleasant, smell being evolved; and the solution, on being allowed to evaporate spontaneously, deposits crystals of mercuric chloride.

Nitric acid (1 vol. acid of sp. gr. 1·42 to 3 vols. water) dissolved it

readily on boiling, red fumes being evolved. No crystals were deposited on cooling, but when a more dilute acid consisting of 1 vol. of the concentrated acid to 4 vols. of water was employed, the substance dissolved somewhat readily on boiling; and the solution, after being filtered and left to cool, rapidly deposited small but very brilliant crystals, which were washed with alcohol and water and dried over sulphuric acid.

Two separate quantities were thus prepared. Under the microscope the crystals are seen to consist of well-developed six-sided tables, and with the polariscope they exhibit beautifully the colours due to double refraction. When mixed with a few grains of sand and struck with a hammer, the substance detonates. When placed in an air-bath, the temperature of which is quickly raised, it explodes at 129—130°, giving off red fumes. If, however, the temperature be raised very slowly, the substance can be decomposed without any explosion, and a residue is left consisting apparently of oxide and nitrate of mercury.

The crystals were powdered cautiously in an agate mortar and again dried over sulphuric acid. A combustion with oxide of copper was made in each case, the front part of the tube in which the mercury had collected being then cut off. Great care was necessary to prevent a minute quantity of mercury from condensing in the sealed end of the combustion-tube, probably in consequence of the large quantity of mercury vapour relatively to the carbonic acid, &c., produced in combustion; and this is probably the reason that the mercury determinations obtained by this process are slightly lower than those in which it was estimated as mercuric sulphide.

This was done in each case, the substance being dissolved in dilute hydrochloric acid, warmed gently, and saturated with hydric sulphide. The mercuric sulphide so obtained was oxidised with fuming nitric acid and hydrochloric acid, and the sulphur determined as barium sulphate. This was then subtracted from the total mercuric sulphide obtained.

Nitrogen was determined by Dumas' method, the modified apparatus for collecting the gas devised by Groves (*Chem. Soc. J.*, 1880, Transactions, p. 500) being employed and found to be very convenient.

The following results were obtained:—

I. On burning with oxide of copper—

0·953 gram gave 0·034 gram water, 0·107 carbonic acid, and 0·7248 mercury.

0·9523 gram gave 0·8455 gram HgS.

0·8259 „ HgS gave 0·8202 gram $BaSO_4$.

0·9458 „ gave 27·9 c.c. nitrogen at 18·7° and 764·5 mm.

II. 0·6650 gave 0·0245 H_2O, 0·075 CO_2, and 0·5042 Hg.

1·0135 gram gave 0·902 gram HgS.
0·8782 „ 0·8910 „ $BaSO_4$.
0·9268 „ 27·6 c.c. N at 18·1° C. and 751 mm.

	I.		II.	
Carbon	3·06		3·07	
Hydrogen	0·39		0·40	
Nitrogen	3·41		3·40	
Mercury	76·05	76·67 (as HgS)	75·82	76·58 (as HgS).

In preparing the substance, as originally described by adding alcohol to the nitric acid solution of mercury after the removal of the first crystallisations, a crop of very beautiful feathery plate-like crystals was obtained, which gave on analysis the following numbers:—

0·9398 gram gave 0·0317 gram H_2O and 0·1085 gram CO_2.
1·0258 grams „ 0·9101 „ HgS.
0·8931 gram HgS gave 0·8869 gram $BaSO_4$.
1·0655 grams gave 31·7 c.c. N. at 16·8° C. and 753·5 mm.

C = 3·15.
H = 0·37.
N = 3·42.
Hg = 76·58 as HgS.

This is obviously the same substance as that obtained by recrystallisation from dilute nitric acid.

An experiment was made to determine whether the substance could be prepared without heat. 20 grams of mercury were dissolved in 184 c.c. of HNO_3 of sp. gr. 1·3, and allowed to stand until colourless; 300 c.c. of pure alcohol were then added, and the mixture left at rest. After about 36 hours, beautiful feathery crystals began to form. They were collected, washed with alcohol and water as before, and on analysis gave the following numbers:—

0·5433 gram gave 0·0163 gram H_2O, 0·0605 gram CO_2, and 0·4140 gram Hg.
0·7855 gram gave 0·6987 gram HgS.

C = 3·03.
H = 0·33.
Hg = 76·06; 76·68 as HgS.

This again is clearly the same compound, and in appearance it is not distinguishable from the last described.

Collecting these results, we have—

	I.	II.	III.	IV.	Average.
Carbon	3·06	3·07	3·15	3·03	3·08
Hydrogen	0·39	0·40	0·37	0·33	0·37
Nitrogen.....	3·41	3·40	3·42	—	3·41
Mercury (mean)	76·36	76·20	76·58	76·37	76·38

This corresponds very closely with the empirical formula $C_2H_2Hg_3N_2O_8$:—

	Found.	Calculated.	Difference.
Carbon	3·08	3·06	+ 0·02
Hydrogen.....	0·37	0·25	+ 0·12
Nitrogen	3·41	3·58	− 0·17
Mercury.....	76·38	76·72	− 0·34
Oxygen (by diff.)	16·76	16·39	+ 0·37

and the agreement is still closer if the determinations of mercury as HgS be considered the more correct.

The compound may be regarded as the nitrate of a dyad radical, consisting of acetylene combined with mercury and mercuric oxide $(C_2H_2Hg_3O_2)''(NO_3)_2$.

Comparing this formula with Gerhardt's, it is seen that the latter chemist found one atom less of oxygen than I have found, and that the formula ascribed by him to the compound cannot be correct; probably because his substance was not pure, not having been recrystallised.

Taking this formula as a basis, the following experiments were made:—

Some of the nitrate was very finely powdered and digested with an equivalent quantity of pure potassium hydrate dissolved in water. It was then collected on a filter and washed. The filtrate, on evaporation, deposited crystals of potassium nitrate. The substance on the filter was dried over sulphuric acid in a vacuum, and an analysis made.

0·5453 gram gave 0·0365 gram H_2O, 0·0695 gram CO_2, and 0·4689 gram Hg.

	Found.	Calculated for the formula $(C_2H_2Hg_3O_2)''(HO_2)$.	Difference.
Carbon	3·47	3·46	0·01
Hydrogen....	0·74	0·58	0·16
Mercury	85·99	86·60	0 61

This reaction may be expressed by the equation—

$$(C_2H_2Hg_3O_2)''(NO_3)_2 + 2KHO = (C_2H_2Hg_3O_2)''(HO)_2 + 2KNO_3,$$

analogous to the decomposition of an inorganic salt by KHO.

The substance still contained a trace of NO_3.

This hydrate does not lose weight appreciably at 100°. Between 115 and 120°, it loses most of its water, but at the same time undergoes partial decomposition, and turns black.

At a higher temperature it gives off a most penetrating and unpleasant odour. If placed in a test-tube and heated in the flame of a Bunsen burner, it decomposes with a slight explosion.

Some of the recrystallised nitrate was powdered as finely as possible and suspended in water. A solution of neutral potassium oxalate was then added and the mixture digested for some days at the ordinary temperature. Next it was gently warmed, and afterwards collected on a filter-paper and washed.

On burning it with copper oxide, the following numbers were obtained:—

0·787 gram gave 0·0245 gram H_2O, 0·175 gram CO_2, and 0·6315 gram Hg.

		Calculated for the formula $(C_2H_2Hg_3O_2)C_2O_4$.
Hydrogen	0·34	0·26
Carbon	6·07	6·43
Mercury.....	80·24	80·42

The following equation shows the manner of formation of this compound:—

$$(C_2H_2Hg_3O_2)''(NO_3)_2 + K_2C_2O_4 = (C_2H_2Hg_3O_2)''C_2O_4 + 2KNO_3.$$

This oxalate, when exposed tc direct sunlight, rapidly becomes of a dark-brown colour.

Some of the nitrate was reduced to an exceedingly fine powder and suspended in water. Hydric sulphide was then passed through the liquid. A strong smell of mercaptan, probably ethylene sulphydrate, was developed, and the black substance produced was found, as pointed out by Gerhardt, not to be pure mercury sulphide, but to contain, after repeated and prolonged treatment, considerable quantities of carbon and hydrogen.

The precipitate is probably at first $(C_2H_2Hg_3O_2)''(HS)_2$, and subsequently decomposes, with formation of HgS and ethylene sulphydrate:—

$$(C_2H_2Hg_3O_2)''(NO_3)_2 + 5H_2S = C_2H_6S_2 + 3HgS + 2HNO_3 + 2H_2O.$$

When dried, it retained a strong smell of mercaptan, and was of an exceedingly greasy character, showing great aversion to becoming wetted by water.

When the finely-powdered nitrate was suspended in absolute alcohol and H_2S passed through the liquid, nearly pure mercury sulphide was obtained.

When H_2S was passed through the hydrochloric acid solution of the nitrate, the precipitate obtained was found on analysis to be free from carbon and hydrogen, and to consist of pure mercury sulphide.

If the nitrate be warmed with a mixture of nitric acid and alcohol similar to that employed in its production, but to which a few drops of fuming nitric acid have been added, it is converted into fulminate of mercury.

Note by Dr. Debus.

The compounds described in this paper and investigated with great care by Mr. Cowper may be regarded as belonging to the type glycol.

$(C_2H_4)''(OH)_2$.	$(C_2H_2Hg_3O_2)''(OH)_2$.
Glycol.	Base.
$(C_2H_4)''(NO_3)$.	$(C_2H_2Hg_3O_2)''(NO_3)_2$.
Ethylene nitrate.	Nitrate.
$(C_2H_4)''C_2O_4$.	$(C_2H_2Hg_3O_2)''C_2O_4$.
Ethylene oxalate.	Oxalate.

Our knowledge of these bodies is not yet sufficiently advanced to determine the constitution of the radical $C_2H_2Hg_3O_2$ with any great degree of probability. According to theory, two or three structural formulæ may be assigned to it. The most simple view is to regard it as a compound of 1 molecule of acetylene with 1 molecule of mercurous and 1 molecule of mercuric oxide, analogous to similar compounds of acetylene with copper and silver oxides.

XL.—*On the Action of Bacteria on Gases.*

By Frank Hatton.

These investigations were made with a view to ascertain the action of various gases on the increase and life of bacteria; also to see what effect these organisms exerted on the gases in which they were placed.

Method of Experiment.—The bacteria were obtained by shaking up fresh meat and water in a bottle; the extract was then filtered carefully, and put aside until it became full of bacteria; this generally took a day to a day and a half in cold weather. When full of life the solution was ready for experimenting. The experiments were all performed over mercury, and in inverted *bolt-head* receivers. The

figure is a rough sketch of the arrangement. *a a'* was the gas under investigation, *b' b* the meat-solution containing bacteria. The shaded part *c* was mercury, F was a bottle which held the bolt-head when not under manipulation. The neck of the bottle during the progress of the experiment stood in mercury in the bottle.

For manipulation, such as getting a specimen of the meat-solution for examination under the microscope, or of pumping out the gas for analysis, the receiver was taken to a large deep mercury trough. A sample of the liquid was taken every day for examination under the microscope for this purpose; the arrangement shown in Fig. 2 was

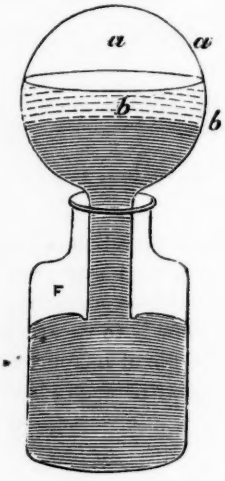


FIG. 1

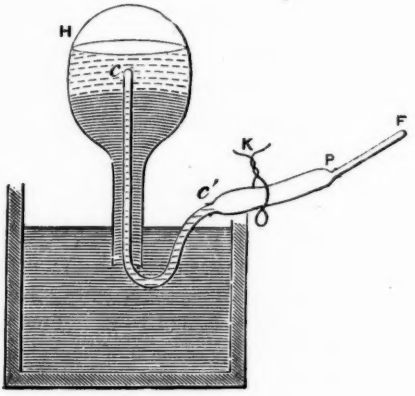


FIG. 2.

employed. A piece of glass tubing, *c c'*, bent as indicated, has an indiarubber joint, P, provided with a spring clip, K; another piece of glass tubing, F, serves as a mouthpiece. The whole of the tube is first filled with mercury, and then the end, *c*, is inserted under the mouth of the flask containing the bacteria. The required amount of the liquid in H is then sucked into *c*, and the tube is withdrawn with the sample in it.

In order to collect the gas from H for analysis a similar apparatus was used. The tubing was capillary, and the gas was pumped out by means of a Sprengel pump.

Bacteria and Air.—The bacteria in the meat-solution were very lively and numerous at the time of introduction of the air. The first experiment was continued seven days before an analysis of the gas

was made. The bacteria were examined daily, and on each of the seven days were found to be very lively and numerous. The temperatures ranged from 20·0° to 17·0°. The solution showed but little change, a large absorption of gas, however, took place. After the first analysis the experiment was continued seven more days, and the bacteria lived well during the whole of this time.

Results of analysis:—

	Original air.	After standing 7 days.	After standing 14 days.
CO_2	0·08	7·85	10·11
O	20·90	0·00	0·00
N	79·02	92·14	89·89
	100·00	99·99	100·00

It will be observed that there was a large absorption of oxygen which did not again appear as CO_2. This is perhaps mainly to be attributed to the cool and gloomy weather, as an experiment made during a rather hot and sunny week, but otherwise under the same conditions as the previous one, gave on the 8th day the following figures:—

CO_2	17·02
O	0·13
N	82·66
	99·99

The temperatures in this case ranged from 24° to 26°. Here also, however, there was an absorption of oxygen which did not again appear as CO_2.

Hydrogen.—The hydrogen passed up into the meat-solution was very pure; it contained 99·98 per cent. of H.

The experiment lasted for nine days, during which time the bacteria lived and flourished well, became very numerous, and were at all times very lively. The temperatures varied from 17° to 24°.

There was a slight absorption of gas, and the colour of the meat-solution changed from pale red to very dark blood-red.

Analyses of the gas on the 9th and 14th days gave:—

	9th day.	14th day.
CO_2	0·24	0·34
H	98·98	98·94
	99·22	99·28

The experiment was continued for four days more, during which

time the bacteria lived well and became very numerous. The temperatures varied from 23—25°. It was expected that some marsh-gas would be formed in the experiment, but although special care was taken in the analysis no trace was detected.

Pure Oxygen.—The gas employed was quite pure. The meat-solution was crammed with bacteria. The experiment lasted six days before analysis of the gas was made, and during this time the bacteria lived well and were very lively and numerous. The colour of the solution gradully faded away during the experiment, and a considerable absorption of gas took place.

Temperatures: 18·0—21·0°.

Analysis of gas on the 7th day gave:—

	7th day.	10th day.
CO_2	27·14	29·98
O	72·82	70·02
	99·96	100·00

The experiment was then continued for four days more. The solution became almost colourless. The bacteria continued to live and increase. The temperatures ranged from 23·0—26·0°. On the 20th day the bacteria were still alive and very numerous, and would have been so no doubt for some considerable period, but as the experiment appeared conclusive it was discontinued. More than one-fifth of the oxygen originally present was converted into CO_2 in 15 days, and in time the whole would have been in this way used up.

Carbonic Oxide Mixture.—A mixture of gases obtained by acting on potassic ferrocyanide with sulphuric acid was employed, after washing through several bulbs of potash-solution.

This mixture gave the following figures on analysis:—

CO	46·94
CO_2	1·27
O	1·27
N	50·51
	99·99

The experiment was continued for 14 days, during which time the bacteria lived and flourished very well. There was a slight evolution of gas on certain days. The temperatures ranged from 18·0° through 20·0°, 21·0°, 23·0°, 25·0° to 26·0°, which was the highest noted.

An analysis of the gas was made on the 14th day, with the following results:—

CO_2	17·77
CO	0·55
H	7·58
CH_4	2·50
N	71·57
	99·97

It will be seen from this that bacteria can live in a gas containing a large percentage of CO without this gas having any effect upon them at all; also that the CO becomes partly converted to CO_2, the rest displacing the dissolved atmospheric air present in the bacteria solution. Marsh-gas and hydrogen are formed probably from the decomposition of animal matters under the peculiar conditions of the experiment.

Cyanogen.—The gas was prepared by heating pure and dry mercuric cyanide; the gas employed contained 0·02 per cent. of N. The experiment lasted 12 days. The notes made as to the condition of the bacteria from day to day, with the temperatures, were as follows:—

1*st day.* Bacteria not so numerous, but many alive and moving. Colour of the solution changed from red to dark brown or almost black. Brown matter deposited, in which many bacteria appear imbedded, 20·0°.

2*nd day.* Solution turned quite black and thick; a very large absorption of gas; a few bacteria still moving, 20·0°.

4*th day.* Solution very black, some still moving in the thick solution, 20·0°.

5*th day.* Many still alive. Slight increase in the volume of the gas remaining standing over the solution, 22·0°.

6*th day.* Same conditions as on 5th, 21·0°.

8*th day.* Further generation of gas; bacteria much brisker in movements and more numerous, 25·0°.

12*th day.* Bacteria quite numerous and lively. Sun out, 26·0°.

Analysis of gas on the 15*th day* gave the following results:—

	15th day.	Second experiment. 11th day.
CN_2	5·35	0·30
CO_2	57·59	85·13
O	2·24	0·60
N	34·79	14·03
	99·97	100·06

In a second experiment with cyanogen containing 1·45 per cent. of N the results were similar. The analysis of the gas on the 11th day is given in the above table. The analysis by absorption alone gives 85·34 per cent. CO_2 and $(CN)_2$, 0·50 O, and 14·06 N.

It appears from these results that cyanogen is fatal to bacteria as long as it exists in the solution in *the form of cyanogen;* but the well-known decomposition of cyanogen into ammonic salts and azulmic acid, soon sets in, and the bacteria assist this decomposition. The germs, as the cyanogen disappears, revive, especially in direct sunlight, and after a few days recover and again become numerous and lively, in spite of the fact that the solution is full of a black compound (paracyanogen ?).

The cyanogen moreover displaces the dissolved gas in the solution, and a little oxygen is always detected in the resulting gas on analysis. Free nitrogen in considerable quantity, derived either from the solution or from the decomposition of the cyanogen, is found, and also a large quantity of CO_2.

Sulphurous Anhydride.—The gas was prepared by heating copper turnings and strong sulphuric acid together; as passed up into the meat solution it was quite pure, being all absorbed by potassic bichromate solution.

The experiment lasted eight days before the gas was analysed. On the first day the colour of the solution had changed from dark red to pale red, and on the second day it was quite bleached. Large quantities of SO_2 had gone into solution, and in fact the meat-solution was saturated with the gas. There was, however, a considerable volume of gas standing above the liquid. During the first eight days the bacteria lived and appeared but little affected by the gas; they were all at times numerous and lively.

Temperatures: 20·0°, 20·0°, 19·5°, 20·0°, 21·0°, 23·0°, 19·5°, 24·0°.

Two analyses of the gas were made on the 8th day.

	a.	*b.*
CO_2	7·87	7·60
O	0·00	0·00
N	2·13	2·38
SO_2	90·10	90·02
	100·00	100·00

The sulphurous anhydride was estimated by absorption with potassic dichromate solution. From these analyses it will be seen that the sulphurous anhydride has displaced a quantity of the air dissolved in the meat-solution, and this accounts for the presence of nitrogen.

The CO_2 may also have been derived in this manner; although it might have been generated by the bacteria.

The bacteria were examined on the 15th day, when the solution was quite bleached, and were found to be still alive in the strongly acid liquid. Temperature 21·0.°

Nitrogen.—The gas was prepared by heating a mixture of dry NH_4Cl, and NOKO. The gas as passed up into the meat-solution had the following percentage composition:—

	a.	*b.*
CO_2	5·90	5·64
O	1·11	1·22
N	92·99	93·14
	100·00	100·00

The solution preserved its colour, the germs lived well, being very numerous and lively throughout the whole of the experiment.

Temperatures: 20·0°, 19·5°, 20·0°, 21·0°, 23·0°, 21·0°, 24·0°.

An analysis of the gas on the 7th day gave—

CO_2	8·25
O	0·00
N	91·74
	99·99

The experiment was continued till the 20th day.

The condition of the bacteria was apparently unchanged, and the solution preserved its colour well.

This is therefore the ordinary air reaction.

Nitrous Oxide.—The gas was prepared by heating ammonic nitrate, and was passed directly into the meat-solution.

An analysis gave the following results:—

ON_2.....	99·94
Residual gas (N) ..	00·06
	100·00

The bacteria were quite unaffected by the presence of the gas, except perhaps that they increased and lived better than in common air.

The temperatures alternated between 25·0° down to 18·5°.

An analysis made on the 7th day gave the following percentages by volume:—

ON_2	95·75
CO_2	1·06
N	3·18
	99·99

The presence of CO_2 and N may be accounted for in two ways. There may have been a reducing action, whereby ON_2 was transformed into CO_2 and free N, or perhaps the gases were derived from the solution, being expelled from it by the more soluble ON_2. As may be expected from foregoing results, the germs were *quite* unaffected by the gas.

Carbonic Anhydride.—The gas was prepared from pure calcic carbonate and pure HCl, it was passed first through distilled water, and then through SO_2HO_2 and pumice. The whole of a specimen volume, collected while the gas was being passed up into the meat-solution, was absorbed by KHO. The bacteria during the experiment were in a flourishing condition.

Temperatures: 22·0°, 26·0°, 23·0°, 25·0°, 25·0°, 25·0°, 21·0°, 20·0°, 24·0°.

Analysis of the gas on the 9th day:—

CO_2	98·12
N	1·87
	99·99

The usual hypothesis of the nitrogen being expelled from the solution by the more soluble CO_2, will here explain the presence of this gas, although it may have been given off by the bacteria.

Sulphuretted Hydrogen.—The only fact to be placed on record in connection with this gas and bacteria, is that during 15 days the bacteria were both numerous and lively. The solution turned a dirty green colour, and became very thick. The temperatures ranged from 26·0° to 18·5° lowest. (The gas was lost during the collection of a sample for analysis.)

Bacteria and Gas from the Electrolysis of Water.

The gas was generated by decomposing acidulated water by a current from four Groves' cells. The operation was performed in the well known apparatus (Bunsen's) for generating the gas used for combustion mixture in gas analysis. Although the apparatus had been working for over half an hour before any of the gas was passed up into the meat-solution, and a sample taken for analysis, it was

found to be by no means pure. I always found traces of free oxygen in excess of that required to combine with the H, and also small quantities of nitrogen present.

An analysis of the gas employed was made with the following results:—

	H_2	66·17
	O	31·08
Air	O	0·48
	N	2·26
		99·99

During seven days the bacteria were in a very flourishing condition. There was no absorption, and no perceptible evolution of gas. The red colour of the solution remained unchanged. Temperatures: 20·0—25·0°.

An analysis on the 7th day gave the following percentages by volume:—

CO_2	20·83
H	76·64
CH_4	0·40
N	2·10
O	0·00
	99·97

It will be observed that oxygen has been again absorbed, and the main part of the free oxygen converted into CO_2, only 10 per cent. remaining in the solution practically unaffected.

There was a slight evolution of nitrogen dissolved in the meat-solution. The apparent increase in the percentage of free hydrogen is due to the removal of the oxygen and its non-appearance as CO_2.

Coal Gas and Bacteria.—The coal gas was not collected directly from the pipe, as there was not enough pressure to drive out the mercury. A tube was attached to the pipe, and connected with a Sprengel pump, and the gas collected in the usual manner.

During the first six days the bacteria were very lively and numerous. There was a slight absorption of gas, and the solution became darker. Temperatures: 20·0—26·0°. The bacteria lived well during the 15 days this experiment lasted.

The results placed side by side are as follows:—

	Before.	After 7 days.	After 15 days.
CO_2	0·05	5·49	7·31
O	0·00	0·00	0·00
C_nH_{2n}	4·48	4·40	4·34
CH_4	46·34	39·91	41·98
H	40·37	39·90	39·67
CO	6·32	2·72	0·00
N	2·43	7·52	6·71
	99·99	99·94	100·01

The variations in the percentage of CH_4 in this experiment are perhaps due to the variation in the quantities of CO, CO_2, and N. The hydrogen remains practically constant, the CO entirely removed, and converted into CO_2, the nitrogen increases. The bacteria were quite unaffected by the presence of the gas, and continued to live and flourish well.

Urea and Phosphate of Potash Solution.

A solution was made containing 0·9780 gram of pure urea to 100 c.c. of boiled distilled water, and a little pure phosphate of potash. Three drops of meat-solution full of bacteria were added, and the solution transferred at once to the mercury trough, and so to the top of the bolt-head. The solution and mercury completely filled the flask, and no trace of air was admitted. There was also *no air* in the liquid, and only the minute quantity contained in the three drops of bacteria solution.

The experiment was continued for 14 days. The solution remained clear; gas was evolved in small quantity during the whole of the experiment. The bacteria did not increase in numbers very largely; but they lived all the time, and were present in considerable quantities.

Temperatures: 18·5°—26·0°.

The composition of the gas given off during these 15 days was as follows:—

CO_2	0·53
O	2·64
N	96·82
	99·99

Thus the gas is almost pure nitrogen, containing a small quantity of O and CO_2; a curious decomposition of urea, effected by bacteria.

Spongy Iron and Bacteria.—20 grams of spongy iron were put into a solution crammed with bacteria, and a small volume of air, of which an analysis had previously been made, let up.

The air before gave—

CO_2	0·09
O	20·90
N	79·01
	100·00

Up till the 3rd day the bacteria were alive, and the colour of the solution green. No bacteria were observed at all on the 4th day. No oxidation of the iron was noted.

The results of an analysis on the 5th day gave the following figures:—

CO_2	0·26
O	0·00
N	99·74
	100·00

Spongy iron is therefore very fatal to bacteria. The air is changed, oxygen entirely absorbed, and also CO_2. Nitrogen is left.

Nitric Oxide, N_2O_2.—The gas was prepared by acting on Cu with nitric acid, and allowing all the air to be displaced.

The gas as employed had the following composition:—

	a.	*b.*
N_2O_2	68·80	68·58
N	31·19	31·41
	99·99	99·99

For 10 days the bacteria remained and lived well.

Temperatures: 21·0°, 23·6°, 24·8°, 20·7°, 20·0°, 19·8°, 20·9°, 21·0°, 19·9°, 23·0°.

Analysis of the gas on the 10th day:—

CO_2	12·86
O	0·00
N	35·89
N_2O_2	51·24
	99 99

In this case the bacteria were quite unaffected by the gas, and the N_2O_2 itself suffered partial decomposition. Nitrogen was liberated from it, and the O combined with some carbon of the meat-solution to form CO_2.

Acetylene, C_2H_2.—This gas was prepared by acting on acetylide of copper with HCl, and warming very gently.

According to the reaction—

$$\begin{Bmatrix} C_2'Cu_2'H \\ O \\ C_2'Cu_2'H \end{Bmatrix} + 4HCl = 2C_2H_2 + 2'Cu_2'Cl_2 + OH_2,$$

as employed in the experiment, the gas had the following composition:—

	By absorption.	By explosion.
C_2H_2	99·64	99·18
N.....	0·36	0·82
	100·00	100·00

During 10 days the experiment was continued, the bacteria lived and appeared quite unaffected.

Temperatures: 21·0—26·0°.

An analysis of the gas on the 10th day gave—

CO_2	1·86
O	0·00
C_2H_2	93·47
N	4·66
	99·99

In conclusion, it may be stated that salicylic acid, strychnine, morphine, narcotine, and brucine, are all *without any effect upon* bacteria even *when quite large* quantities are put into the solution containing the germs.

It was also noted that phenol, spongy iron, alcohol, and permanganate of potash destroyed bacteria with great rapidity.

In conclusion, I take the opportunity of expressing my sincere thanks to Professor Frankland for his invaluable assistance and kind advice, without which I could never have hoped to bring to a successful termination the long series of experiments here described.

XLI.—*On the Oxidation of Organic Matter in Water by Filtration through various Media;* and *On the Reduction of Nitrates by Sewage, Spongy Iron, and other Agents.*

By Frank Hatton.

In a paper read by Dr. Frankland to the Chemical Society (*Chemical Society's Journal*, July, 1880), the question of oxidation of organic matter in water was treated of at length. Dr. Frankland showed

that the alleged self-purification of rivers by flow, was to be accounted for by other reasons than those advanced in a paper by Dr. Tidy (*Chem. Soc. Journal*, May, 1880). In one instance in which the Thames was referred to as an example of oxidation by flow, Dr. Frankland says:—"For several miles above Hampton, the Thames runs through a vast deposit of flint-gravel and sand, which sops up its water like an immense sponge, restoring it again to the river, either near the place of absorption, after floods, or below the next lock in dry weather. Thus vast volumes of Thames water are purified by this exhaustive filtration through gravel and sand, that is to say, by oxidation in a porous medium, which I have again and again shown to be the most potent agency in nature for the removal of organic matter in water."

Bearing in mind the previous experiments on the oxidation of organic matter in water by filtration through various media (published in the Sixth Report of the Rivers Pollution Commissioners), I have investigated the influence of intermittent filtration through sand on animal and vegetable matters dissolved in water. The reduction of nitrates by sewage and other agents, and the influence of filtration through spongy iron on animal and vegetable matters in water, were also subjects of my investigation.

The inquiry divides itself therefore into three heads, which may be stated thus:

1. On the influence of intermittent filtration, through sand, on animal and vegetable matters dissolved in water.
2. On the reduction of nitrates by sewage and other agents.
3. On the influence of filtration through spongy iron on animal and vegetable matters dissolved in water.

Throughout the whole of these experiments, wherever practicable, estimations of the amount of dissolved atmospheric air contained in the water or mixture experimented upon, have been made. The method employed for these observations was that recommended by Miller in his "Organic Chemistry."

1. *The Influence of Intermittent Filtration through Sand on Animal and Vegetable Matters dissolved in Water.*

For the purpose of studying this branch of my subject, a glass tube, 14 feet long and $3\frac{1}{2}$ inches in diameter, was fixed in a vertical position and 12 feet of the whole length was filled with sand. At the foot of the tube a smaller glass tube was let in for the purpose of allowing the water to filter through, drop by drop. To filter four litres of water took a whole day, the sand and apparatus being repeatedly washed with distilled water, until the filtered water contained no

estimable amount of organic impurity, and no nitrogen as nitrates or nitrites.

For estimation of dissolved atmospheric air after filtration, the sample, with the exception of the first experiment, was always collected directly from the tube into a bottle filled with mercury and standing inverted in a mercury trough.

For the first experiment a sample of natural peaty water was diluted with its own volume of distilled water and filtered through 96 feet of sand. This experiment occupied eight days, the water being passed through once daily.

The following were the results obtained:—

Dissolved atmospheric air *before filtration.*

From 345 c.c. of water (345 c.c. being the capacity of the bulb employed for boiling out) 6·9367 c.c. of air were obtained, which corresponds to 20·106 c.c. air per 1000 c.c. of water.

The percentage composition of the gases from analysis was:

			Parts per 100,000.
CO_2	1·98	Organic carbon	2·912
O	31·96	Organic nitrogen	0·167
N	66·05	N as nitrates and nitrites..	0·000
	99·99		

After filtration through 96 feet of sand an analysis of dissolved atmospheric air gave the following figures:—

Volume of air from 345 c.c. of the water 7·7920, or 22·58 c.c. per 1000 c.c. water.

The percentage composition was:—

			Parts per 100,000.
CO_2	6·55	Organic carbon	1·385
O	31·53	Organic nitrogen	0·144
N	61·92	N as nitrates and nitrites..	0·007
	100·00		

It will be observed from these results that the decrease of organic carbon by filtration through 96 feet of sand is 1·527, or 0·00015 per cent.

The organic nitrogen decreased 0·023, or 0·0023 per cent.

The increase in nitrogen as nitrates and nitrites was only 0·007.

The CO_2 in the dissolved air increased 4·56 per cent., and the water became aërated, 3·04 c.c. per 1000 c.c. of the water used.

These results show that the organic nitrogen of peat is very little affected by filtration through sand, and that a peaty water would have

to filter through immense depths of porous material, before all the nitrogenous matters would be converted into their inorganic representatives.

The next experiment was made with a view to ascertain whether the presence of a nitrifying agent in the water would determine the nitrification of the peat. It was made with the same peaty water, but with the addition of some stale urine. The mixture contained $1\frac{1}{4}$ litres peaty water, $1\frac{1}{4}$ litres distilled water, and 2·5 c.c. of stale urine. This mixture gave the following results :—

An analysis of dissolved atmospheric air showed that the mixture contained 7·3917 c.c. of air per 345 c.c. water, or 21·42 c.c. air per litre of the mixture.

Percentage composition of the gases :—

			Parts per 100,000.
CO_2	10·07	Organic carbon	5·444
O	30·09	Organic nitrogen	1·353
N	59·84	N as nitrates and nitrites..	0·007
	100·00		

This mixture was then passed through the sand eight times, and so filtered through 96 feet of porous material.

After filtration an estimation of dissolved atmospheric air gave 7·3317 c.c. of air from 345 c.c. of the filtered mixture; or 21·25 c.c. air per 1000 c.c. of the water.

Percentage composition of the gases :—

			Parts per 100,000.
CO_2	7·56	Organic carbon	2·013
O	30·90	Organic nitrogen	1·199
N	61·54	N as nitrates and nitrites..	0·044
	100·00		

The temperature during the filtration of this last mixture was rather low (average from 16·5—18·5° C.). Suspecting that the organic nitrogen was converted into ammonia, another experiment was made with a stronger mixture of urine and peaty water.

This second mixture consisted of peaty water 2 litres, distilled water 2 litres, and stale urine 5·0 c.c.

An analysis of dissolved gases gave the following percentage composition :—

CO_2	10·09
O	29·19
N	60·72
	100·00

The volume of air from 345 c.c. was 7·4390,
Or per 1000 c.c. of the water, 20·73 c.c. of air.
The mixture also contained—

	Parts per 100,000.
Organic carbon	8·003
Organic nitrogen	1·457
Nitrogen as nitrates and nitrites..	0·027
Ammonia	0·088

The experiment was performed under conditions similar to those of the previous one, but at a higher average temperature, the range being 20·0—26·0° C.

The nitrogen as nitrates and nitrites was estimated daily after each filtration of 12 feet, so as to observe the increase in nitric nitrogen. These daily observations were made with a standard solution of indigo according to directions given by Warington.

The following table shows the results.

Daily increase of nitrogen as nitrates and nitrites, by filtration through sand of a mixture of peaty water and urine. Taken by the indigo method.

	Nitrogen as nitrates and nitrites per 100,000.
Before filtration.....	0·027
1st day after filtration through 12 feet of sand..	0·027
2nd " " " 24 " ..	0·030
3rd " " " 36 " ..	0·044
4th " " " 48 " ..	0·072
5th " " " 60 " ..	0·090
6th " " " 72 " ..	0·150
7th " " " 84 " ..	0·300
8th " " " 96 " ..	0·750
9th " " " 108 " ..	1·152
10th " " " 120 " ..	1·204
11th " " " 132 " ..	1·204

After filtration of the mixture of peaty water and urine through 132 feet of sand, analysis of dissolved atmospheric air gave the following results :—

CO_2	11·46
O	21·62
N	66·92
	100·00

The volume of dissolved atmospheric air from 345 c.c. of the mixture, after filtration through 132 feet of sand, was 7·4547,

Or per 1000 c.c. of the mixture, 20·73 c.c. of air.

The mixture after filtration through 132 feet of sand also yielded on analysis the following results :—

Organic carbon	0·807
Organic nitrogen	0·164
Nitrogen as nitrates and nitrites..	1·204
Ammonia	0·218

From the previous analysis of the mixture of peat and distilled water given in the first of my experiments, I am enabled to arrive at the following data connected with the experiment now being considered :—

The organic carbon due to urine in this mixture was 5·091.

The organic carbon due to peat was 2·912.

The organic nitrogen due to urine, or animal organic nitrogen, 1·290.

The organic nitrogen due to peat or vegetable organic nitrogen, 0·167.

It will be seen that the total decrease in organic carbon was 7·196 pts. per 100,000.

The total decrease of organic nitrogen 1·293 pts. per 100,000.

The organic nitrogen left unoxidised during the filtration was 0·164, or *almost exactly* the amount of organic nitrogen due to peat.

From an inspection of the results of the analysis of the first peaty water experiment, it will be seen that the results just stated are very easily arrived at. For instance, the organic nitrogen from a previous analysis of the same peaty mixture was 0·167. After the addition of the 5 c.c. of urine the organic nitrogen is increased to 1·437. Therefore by subtracting, this gives 0·167 pt. vegetable organic nitrogen, and 1·290 pts. animal organic nitrogen per 100,000 pts. of the mixture. The total decrease in organic nitrogen was 1·293 pts. per 100,000 ; and subtracting this from the amount originally present, gives 0·164 pt. per 100,000 of unoxidised organic nitrogen, the amount of vegetable organic nitrogen present before the filtration of the mixture being 0·167.

It may therefore be concluded that animal organic matter is quickly oxidised by filtration through sand ; but that vegetable organic matter is not so quickly oxidised, and that peaty organic nitrogen, in the presence of animal organic matter, which is itself undergoing conversion into ultimate inorganic substances, does not, to any considerable extent, become converted into either ammonia or nitrates.

The results obtained from the dissolved atmospheric air experiments are significant. The oxygen has decreased to the extent of 8·56 per cent., and the CO_2 has increased 1·37 per cent., while the general volume of dissolved air curiously enough has become but slightly altered.

In order to ascertain whether the results just stated applied also to other kinds of vegetable organic matter in water, a solution of rape cake, prepared by infusing rape cake in warm water. After it had digested a short time, the whole was filtered through linen. The extract was of a deep brown colour and very frothy, giving off an unpleasant odour. This was diluted considerably, and the following experiments made with it:—

The volume of dissolved atmospheric air, &c., from 350 c.c. was 8·0189 or 22·20 c.c. of air per 1000 c.c. of the solution.

This percentage composition of the air was—

			Parts per 100,000.
CO_2	22·78	Organic carbon	6·532
O	23·63	Organic nitrogen	1·404
N	53·59	N as nitrates and nitrites..	0·035
		Ammonia	0·066
	100·00		

The solution was then filtered nine times through the tube, making 108 feet of sand in all. The temperature average 18·0—20·5° limits. A specimen was taken after each filtration, and the amount of nitrogen as nitrates and nitrites estimated daily by the indigo method.

Table of the Increase of Nitrogen as Nitrates and Nitrites by Filtration of a Solution of Rape Cake through 108 *feet of Sand.*

	Indigo method.	Gas method.
Before filtration	0·040	0·030
1st day after filtration through 12 feet ..	0·040	—
2nd „ „ 24 „ ..	0·040	—
3rd „ „ 36 „ ..	0·075	—
4th „ „ 48 „ ..	0·075	—
5th „ „ 66 ..	0·112	—
6th „ „ 72 „ ..	0·112	—
7th „ „ 84 „ ..	0·112	—
8th „ „ 96 „ ..	0·112	—
9th „ „ 108 „ ..	0·150	0·198

After the filtration through 108 feet of sand, the volume of dissolved atmospheric air from 350 c.c. of the solution was 7·9938, or per 1000 c.c. 22·83 c.c. of air, having the following percentage composition:—

			Parts per 100,000.
CO_2	17·29	Organic carbon	1·088
O	23·02	Organic nitrogen	0·298
N	59·69	Ammonia	1·300
	100·00	N as nitrates and nitrites..	0·150

It will be seen that the oxygen and the CO_2 have decreased, and the nitrogen increased, while the general volume remains the same. All these samples for the estimation of dissolved atmospheric air after filtration were collected over mercury.

The decrease in organic carbon was 5·444. The decrease in organic nitrogen, 1·106 pts. per 100,000. The increase in ammonia, 1·234, corresponding to 1·026 pts. increase in N per 100,000 pts. The increase in N as nitrates and nitrites, 0·115.

From this experiment it will be seen that the oxidation of certain kinds of vegetable matters is rapid. The organic carbon is quickly oxidised. The organic nitrogen is for the most part converted into ammonia.

In order to confirm this last experiment a second one was made with a fresh solution of rape cake, and the following data were obtained:—

Before filtration the volume of dissolved atmospheric air from 340 c.c. was 8·1030, or 23·83 c.c. per litre of the solution, having the following percentage composition:—

			Parts per 100,000.
CO_2	22·10	Organic carbon	8·458
O	24·14	Organic nitrogen	1·970
N	53·76	Ammonia	0·080
	100·00	N as nitrates and nitrites..	0·000

Under circumstances almost exactly similar to those of the last experiment, at an average temperature of 17—21·5°, this mixture was filtered nine times through 12 feet of sand, making 108 feet altogether.

On the completion of the filtration a specimen collected for dissolved air determination gave 7·2450 c.c. of air from 340 c.c., or 21·30 c.c. of air per litre.

The percentage composition was—

			Parts per 100,000.
CO_2	11·76	Organic carbon	2·071
O	22·04	Organic nitrogen	0·293
N	67·30	Ammonia	2·000
	100·00	N as nitrates and nitrites..	0·016

From this it will be seen that the increase in ammonia was 1·920, corresponding to 1·581 pts. of N per 100,000 pts. solution.

The increase in N as nitrates and nitrites, 0·016.

The decrease in carbon, 6·387.

The decrease in organic nitrogen was 1·677.

In the first experiment with rape cake solution, the total loss in organic nitrogen was 1·106 pts. per 100,000, of which 1·026 pts. became ammonia, and 0·115 pt. was oxidised to nitric and nitrous acids (the excess, 0·035 pt., may fairly be stated as experimental error).

In the second experiment the total loss in organic nitrogen is 1·677 pts. per 100,000, of which 1·581 pts. became ammonia, 0·016 pt. becoming oxidised (the error or loss here is 0·090). In the second experiment the dissolved air results show a marked diminution in oxygen.

The increase of the formation of nitrates and nitrites is shown by the following table :—

Nitrogen determined by the Indigo Process.

1st day after filtration		through	12	feet	0·000
2nd	,,	,,	24	,, ...	0·000
3rd	,,	,,	36	,, ...	0·000
4th	,,	,,	48	,, ...	0·010
5th	,,	,,	60	,, ...	0·013
6th	,,	,,	72	,, ...	0·016
7th	,,	,,	84	,, ...	0·016
8th	,,	,,	96	,, ...	0·016
9th	,,	,,	108	,, ...	0·016

2. *On the Reduction of Nitrates by Sewage and other Agents.*

The reduction in the quantity of nitric nitrogen which takes place when fresh sewage is added to a solution of nitre is an observation which has been recorded by the Rivers Pollution Commissioners, but no authenticated experiments have to my knowledge been made on the subject. In the following pages will be found the results of my investigations on the subject.

A solution was made of 0·0853 gram of NO_2KO in distilled water; 5 per cent. of moderately clear fresh sewage was then added. The sewage was full of bacteria.

Before adding the sewage the solution contained :—0·514 pt. of nitrogen as nitrates and nitrites per 100,000, according to the gas method, and 0·526 pt. according to a standard indigo solution.

The mixture was then put into a large stoppered bottle, and agitated

from time to time. Estimations of nitrogen as nitric nitrogen were made daily, at first, and then after at intervals, with the following results:—

Decrease of nitrogen as nitric nitrogen.	Indigo method.	Temp. Centigrade.
1st day after admixture with the sewage..	0·451	18·1°
2nd ,, ,, ,, ..	0·376	21·5
5th ,, ,, ,, ..	0·338	23·0
7th ,, ,, ,, ..	0·338	21·0
8th ,, ,, ,, ..	0·301	23·5
9th ,, ,, ,, ..	0·301	24·0
10th ,, ,, ,, ..	0·370	23·7
11th ,, ,, ,, ..	0·370	22·0
12th ,, ,, ,, ..	0·413	22·5
16th ,, ,, ,, ..	0·450	19·0
30th ,, ,, ,, ..	0·500	21·0

Another experiment was made with a solution containing 0·0835 gram of NO_2KO and 5 per cent. of similar sewage, and the whole mixture kept at 0° C. in an ice safe.

Before adding the sewage the solution contained 0·512 pt. of nitric nitrogen per 100,000 by a gas method experiment, and 0·526 pt. by the indigo process.

The reduction is shown in the following table :—

	Indigo method.	Temp.
1st day after admixture.....	0·451	0°
5th ,, ,, ...	0·413	0
7th ,, ,, ...	0·376	0
9th ,, ,, ...	0·376	3
11th ,, ,, ...	0·313	4
16th ,, ,, ...	0·313	5
30th ,, ,, ...	0·313	0

From these experiments it will be seen that the reduction is very gradual, but is more rapid with a higher temperature. Nitrification of the sewage itself seems to set in in the case of the specimen kept at the temperature of the laboratory after the reduction, and this nitrification was suspended, if not stopped, by the lower temperature.

I next made a solution of nitre containing 0·0745 gram per 2250 c.c. water, and added to this 25 per cent. of fresh clear sewage, containing no nitrates. This was kept in a bottle, which stood neck downwards over mercury. The air standing over the nitre solution and sewage was analysed, and also the dissolved atmospheric air. These experiments were made at the commencement and close of the

observation. A specimen of the liquid for the estimation of nitric nitrogen was removed daily, without letting in air, by an arrangement which has already been described.

The nitrogen as nitrates and nitrites before the addition of the sewage was—

Gas method.	Indigo.
0·406	0·375 pt. per 100,000.

Table of reduction.	Temp.	Indigo process.
2 days after admixture with sewage ..	18·0	0·228
3 „ „ „ ..	21·0	0·150
4 „ „ „ ..	20·0	0·150
5 „ „ „ ..	23·0	0·150
8 „ „ „ ..	24·5	0·150
16 „ „ „ ..	21·7	0·075

At the commencement an analysis of dissolved atmospheric air gave 9·1800 c.c. from 346 c.c. of water, or 26·55 c.c. of air per litre, having the following percentage composition:—

		Air standing above.
CO_2	31·52	0·08
O.....	15·88	20·73
N.....	52·60	79·19
	100·00	100·00

The high percentage of CO_2 is accounted for by the sewage, and also by the fact that the distilled water contained a large volume of CO_2.

After the mixture had stood, with agitation from time to time, for eight days, an estimation of dissolved atmospheric air gave the following data:—

Volume of gas from 345 c.c. = 9·9270, or per litre, 28·77 c.c. of air, having the percentage composition—

		Air standing above.
CO_2	32·52	0·02
O.....	20·37	15·77
N	47·11	84·11
	100·00	100·00

The CO_2 in the dissolved atmospheric air has increased 1·00 per cent., and 0·06 per cent. of this has been absorbed from the air standing over the liquid.

The oxygen in the dissolved atmospheric air has increased 4·49 per cent., while the oxygen in the air standing in the bottle has decreased

4·96 per cent. From this it will appear that during the reduction of nitrates by sewage CO_2 is generated in the liquid, and perhaps free nitrogen given off while oxygen is absorbed. The level of the liquid in the bottle marked from day to day did not alter.

In order to confirm these results, and also to observe the effect of the reduction on a much stronger solution of nitre, I tried another experiment of a similar nature, only with a much stronger solution of nitre.

15 per cent. of thick sewage was added to this solution.

Before the admixture with the sewage the solution gave the following results :—

	Indigo method.	Gas method.
Nitrogen as nitrates and nitrites. .	2·483	2·509

The experiment was performed under the same conditions, and in fact at the same time as the one just described.

An analysis of dissolved atmospheric air, after immediate admixture with the sewage, gave—

Volume of gas from 346 c.c. = 7·8730, or per 1000 c.c. 22·75 c.c. of air.

The percentage composition of which was—

CO_2	30·25
O	17·29
N	52·46
	100·00

The former analysis of the air of the laboratory previously mentioned was taken.

The following table represents the rate of reduction of the nitric nitrogen estimated by the indigo process :—

			Temp.	Parts N per 100,000.
2 days after admixture ..			19·5°	2·483
3	„	„ ..	18·5	1·956
4	„	„ ..	20·0	1·655
5	„	„ ..	22·3	1·505
8	„	„ ..	24·0	1·505
16	„	„ ..	25·0	1·279

The total reduction during 16 days effected by 25 per cent. of thick sewage being 1·204 pts. of nitric nitrogen per 100,000.

In no experiment on the reduction of nitrates by sewage except the first, which was continued for 30 days, was I enabled to observe the subsequent nitrification of the sewage itself after the reduction of the nitric nitrogen.

After this mixture had stood eight days an analysis of dissolved atmospheric air gave from 345 c.c. of the water, 8·9683 c.c. of gas, or 25·99 c.c. per litre.

The percentage composition being—

		Air standing above.
CO_2	28·21	0·60
O.....	21·71	16·51
N.....	50·08	82·89
	100·00	100·00

In this second experiment with the thick sewage sediment oxygen was absorbed, as before, to the extent of 4·42 per cent. in the liquid, and a loss of 4·22 per cent. in the air. But in this experiment CO_2 was given off, or there was at least a loss of 2·04 per cent. of CO_2 in the liquid, and again of 0·52 per cent. of CO_2 in the air standing above. This experiment only shows the difference in the action of clear and thick sewage on nitrates, the reduction in the second case being greater than the former. The fact of free nitrogen being given off cannot of course be established, but it seems a probable and certainly a possible action. The temperatures in both cases were about the same.

The effect of SH_2 on nitrates was next studied. A solution containing 0·0385 gram KNO_3 per 7 litres was made.

The amount of nitric nitrogen per 100,000 pts. was determined, and gave 0·188 by the gas method. 50 c.c. of saturated SH_2 solution was added, and the whole allowed to stand. After immediate admixture, the mixture gave 0·155 pt. of nitrogen per 100,000 pts., which, when the dilution caused by the 50 c.c. of water being added is taken into account, is no reduction at all. When nearly saturated with gas, the solution gave 0·075 pt. of nitric nitrogen; and after standing two days, no nitrates could be detected at all.

A similar experiment gave—

KNO_3, 0·0385 gram.
Before adding SH_2, 0·188.
After adding 20 c.c. SH_2 solution, 0·158.
Saturated and allowed to stand two days 0·000.

From these experiments it seems reasonable to conclude that small quantities of SH_2 do not reduce nitrates; but that when the water is saturated with gas the nitric nitrogen is wholly reduced.

I next tried the effect of shaking up, in a bottle, a solution of nitre with spongy iron. Before adding the spongy iron, an analysis of dissolved atmospheric air gave—

6·8703 c.c. of air from 340 c.c. of solution; or 20·20 c.c. of air per litre of the solution.

The percentage composition being—

CO_2	11·99
O	30·36
N	57·64
	99·99

The large quantity of CO_2 present is accounted for by the fact that distilled water was used, which I always found to contain a large quantity of CO_2.

Estimations of nitrogen as nitrates and nitrites, and of ammonia before the spongy iron was added gave—

Ammonia .... 0·016 part per 100,000.

	Gas method.	Indigo method.
Nitrogen as nitrates and nitrites..	6·059	6·059

The spongy iron was then added, there being 100·0 grams of it in 2 litres of the solution. The bottle filled with the solution stood neck downwards in a mercury cup. The whole was shaken up from time to time. There was no great oxidation of the iron.

After standing 10 days, the results on analysis of dissolved air were :—

6·2873 c.c. of air from 340 c.c., or per litre 18·49 c.c. of air.

Percentages of gases—

CO_2	0·00
O	5·49
N	94·47
	99·96

During the 10 days the experiment lasted, there was a constant evolution of gas, but in quantities too small for analysis. In the dissolved atmospheric air 11·99 per cent. of CO_2, being all that was present, has been absorbed by the iron, the iron becoming carbonate. The oxygen, too, has been greatly reduced, and the gas remaining dissolved is now almost pure nitrogen.

The nitric nitrogen was estimated and found to be—

Indigo process.	Gas process.
3·361	3·360

The ammonia was 1·200 pts. per 100,000. Thus the total decrease in nitrogen as nitrates and nitrites was 2·698; while the total increase in ammonia was 1·184 pts. per 100,000, which corresponds to 0·975 pt.

of N. There is thus a loss of 1·723 pt. of N during the conversion of the nitric nitrogen into ammonia. It is also safe to conclude that oxygen and carbonate of iron can exist together in solution. The spongy iron converts the nitrogen present as nitric nitrogen into ammonia, the bases probably becoming carbonates.

3. *On the Effect of Filtration through Spongy Iron on Animal and Vegetable Matters in Solution in Water.*

I began this subject by first studying the effect of filtration through spongy iron on solutions of nitre.

A solution containing 1·0113 gram of nitre was made. This, before filtration, gave results as follows:—

	Gas method.	Indigo method.
Nitrogen as nitrates and nitrites..	2·648	2·653
Ammonia	0·011.	

The decrease of nitrogen as nitrates and nitrites after each filtration is given in the following table:—

Once through the filter	2·257
Twice through the filter.....	2·030
Three times through the filter (allowed to stand overnight)	0·376
Four times through the filter.....	0·075
Five times through the filter	0·000

The decrease in nitric nitrogen is therefore 2·633.

An estimation of ammonia, after five filtrations, gave 1·840 pts. per 100,000, corresponding to 1·515 pts. per 100,000 of N. There is here again a loss of N during the transformation of nitric nitrogen into ammonia, and in this case the loss is 1·118 pts. per 100,000.

Dissolved atmospheric air estimations were made at the commencement and at the close of the experiment. To collect the sample for the experiment after filtration five times, a tube was attached to the filter and led into the boiling-out flask, itself filled with mercury. By this means all exposure was prevented.

Dissolved Atmospheric Air Results.

Before filtration.	*After 5 filtrations.*
Vol. of air from 340 c.c. OH_2 = 6·9177, or per litre of water = 20·34.	Vol. of air from 340 c.c. OH_2 = 6·4372, or per litre of water = 18·93.
Percentage composition—	Percentage composition—
CO_2 .... 22·60	CO_2 .... 0·00
O ..... 24·42	O ..... 23·30
N ..... 52·98	N ..... 76·70
100·00	100·00

Although there was a marked diminution in O, and the CO_2 had all disappeared, I am confident there would have been a far greater diminution in the volume of gas, had it not been for the unavoidable exposure caused by pouring into the filter for a second filtration and running out. In the second and all subsequent experiments with the spongy iron filter, this exposure was avoided as much as possible by collecting the water, in a bottle closed with a bored cork (with two holes in it), and pouring it into the filter quickly but gently. The following results will show that these precautions were to some extent successful.

Before filtration :—

	Indigo method.	Gas method.
Nitrogen as nitrates and nitrites..	1·986	2·006
Ammonia ..	0·018 per 100,000 parts.	

A second experiment was tried with a fresh solution of nitre in distilled water.

I generally found distilled water to contain about 0·016 of NH_3 and a large quantity of CO_2 in solution.

The solution was then passed through the spongy iron filter eight times.

The decrease of nitric nitrogen per 100,000 is shown by the following table :—

Decrease of Nitrogen after each Filtration.

	Indigo method.	
Before filtration.....	0·006	parts per 100,000.
After one filtration	1·580	,,
After two filtrations	1·200	,,
After three filtrations	0·903	,,
After four filtrations.....	0·602	,,
After five filtrations	0·489	,,
After six filtrations	0·225	,,
After seven filtrations	0·075	,,
After eight filtrations	0·000	,,

Although the reduction has not taken place so quickly in this experiment the result is the same, the total reduction is 2·006 ammonia, after eight filtrations 1·400, corresponding to 1·152 pts. of N. There is here a loss of 0·854 pt. of N during the reduction.

Results of Dissolved Atmospheric Air.

Before filtration.	*After four filtrations.*	*After six filtrations.*
Volume of gas from 340 c.c. 7·6300, or per litre 22·44 c.c. air.	Volume of gases from 340 c.c. 5·455, or per litre 16·04 c.c. air.	Volume of gases from 340 c.c. 5·2079, or per litre 15·31 c.c. air.
Percentage composition—	Percentage composition—	Percentage composition—
CO_2.. 19·89	CO_2 .. 0·00	CO_2 .. 0·00
O.... 27·87	O .... 14·05	O .... 14·02
N.... 52·24	N .... 85·95	N .... 85·98
100·00	100·00	100·00

Although the precautions before referred to were put in force during this experiment, I was unable to reduce the percentage of oxygen below 14·02 per cent. This seems to point again to the fact before stated, that oxygen and carbonate of iron can exist together in solution. On standing, after filtration, most of these solutions deposited oxide of iron.

The effect of filtration through spongy iron on a solution of peat was next tried.

An infusion of peat in hot distilled water was made. The whole was filtered hot through paper, and then estimations of dissolved atmospheric air, and of organic carbon, &c., made.

The following results were obtained:—

Volume of air from 340 c.c.. . 7·267
or per litre of the solution. . 21·37

Percentage composition of gases—

			Parts per 100,000.
CO_2	43·040	Organic carbon	2·296
O	0·006	Organic nitrogen.....	0·650
N	56·953	N as nitrates and nitrites..	0·000
CH_4	0·000	Ammonia	0·144
	99·999		

The solution was then filtered through a spongy iron and gravel filter. It required about 25 minutes for the whole to pass through. The filter was covered and precautions taken for the prevention of the entrance of "blacks" and other organic matter. During the filtration, some slight evolution of gas was observed. This fact was ascertained by thrusting a steel needle into the filter when small bubbles of gas were seen to rise. An attempt to collect any quantity failed.

A sample was collected after each filtration, and an estimation of organic carbon made.

Decrease of Organic Carbon and Nitrogen after each Filtration.

	1.	2.	3.	4.	5.	6.
C ..	1·513	0·484	0·276	0·192	0·075	0·060
N ..	0·414	0·187	0·080	0·028	0·000	0·000

Thus the total decrease in organic carbon by six filtrations is 2·236; the total loss in organic nitrogen is 0·650.

The increase in ammonia was studied after each filtration and is shown in the following table :—

Increase in Ammonia after each Filtraton.

Before filtration.....	0·144 part per 100,000.
Once through.....	0·200 ,,
Twice through	0·437 ,,
Thrice through	0·589 ,,
Four times through	0·750 ,,
Five times through	0·900 ,,
Six times through.....	0·900 ,,

Thus the total increase in ammonia is 0·756, corresponding to 0·622 pt. of N per 100,000; and the total loss of organic N of peat is 0·650. Allowing for experimental error, it is seen that the whole of the organic nitrogen of peat becomes in time ammonia during filtration through spongy iron. There was no nitrogen as nitrates or nitrites after six filtrations.

A dissolved atmospheric air estimation gave—

5·5028 c.c. of air from 340 c.c. of water, or 16·18 c.c. of air per litre.

An analysis of the gas was made, and suspecting that CH_4 might be formed, the O was determined with pyrogallic acid and potash.

CO_2	0·00
O	16·50
N	76·69
CH_4	6·79
	99·98

The results drawn from this experiment are that the organic nitrogen of peat is wholly converted into ammonia; and the organic compounds and substance partly reduced to marsh-gas. No nitric nitrogen is found.

I next tried the effect of filtration on a solution of egg albumin. A portion of the white of an egg was poured into 8 litres of distilled

water. This was then filtered through linen, and estimation of dissolved air and organic carbon, &c., made.

The following results were obtained :—

Volume of dissolved air from 340 c.c., 7·3148, or per 1000 c.c.

Having the following percentage composition :—

			Parts per 100,000.
CO_2	12·40	Ammonia	0·125
O	28·10	N as nitrates and nitrites..	0·00
N	59·49	Organic carbon.....	25·200
	99·99	Organic nitrogen	7·162

This solution was then filtered through the spongy iron filter eight times, and allowed to remain after each filtration all night. It thus took eight days to filter.

The results obtained after filtration are given below :—

Ammonia	0·500
N as nitrates and nitrites	0·000
Organic carbon	0·492
Organic nitrogen	0·220

The decrease in organic carbon was 24·708, and of organic nitrogen 6·942, of which only 0·375 pt. is transformed in ammonia; no nitric nitrogen is formed.

An estimation of dissolved atmospheric air gave—

4·958 c.c. of air from 34 c.c. of water.

An analysis gave the following figures :—

CO_2	0·00
O	13·72
N	85·65
CH_4	0·61
	99·98

The conclusion drawn from the experiments as to the influence of spongy iron on organic matter in water are: 1. That it acts as a very powerful reducing agent on the carbon compounds composing the organic matter dissolved in water. In some cases marsh-gas itself was produced; probably the organic matter was first oxidised to CO_2, and then the action of metallic iron on this gas giving rise to CH_4 by the ordinary decomposition of water. 2. The organic nitrogen is in nearly all cases reduced to ammonia.

XLII.—*On the Modern Development of Faraday's Conception of Electricity.*

By Professor Helmholtz.

[The Faraday Lecture, delivered before the Fellows of the Chemical Society, in the Theatre of the Royal Institution, on Tuesday, April 5, 1881.]

Ladies and Gentlemen,

As I have the honour of speaking to you in memory of the great man, who from the very place where I stand has so often revealed to his admiring auditors the most unexpected secrets of nature, I hope at the outset to gain your assent if I limit my exposition to that side of his activity, which I know the best from my own experience and studies: I mean the theory of Electricity. The majority, indeed, of Faraday's own researches were connected directly or indirectly with questions regarding the nature of electricity, and his most important and most renowned discoveries lay in this field. The facts which he discovered are universally known. Every physicist, at present, is acquainted with the rotation of the plane of polarisation of light by magnetism, with dielectric tension and diamagnetism, and with the measurement of the intensity of galvanic currents by the voltameter, whilst induced currents act on the telephone, are applied to paralysed muscles, and nourish the electric light. Nevertheless, the fundamental conceptions by which Faraday was led to these much admired discoveries, have not received an equal amount of consideration. They were very divergent from the trodden path of scientific theory, and appeared rather startling to his contemporaries. His principal aim was to express in his new conceptions only facts, with the least possible use of hypothetical substances and forces. This was really an advance in general scientific method, destined to purify science from the last remnants of metaphysics. Faraday was not the first, and not the only man, who has worked in this direction, but perhaps nobody else at his time did it so radically. But every reform of fundamental and leading principles introduces new kinds of abstract notions, the sense of which the reader does not catch in the first instance.

Under such circumstances it is often less difficult for a man of original thought to discover new truth than to discover why other people do not understand and do not follow him. This difficulty must increase in Faraday's case because he had not gone through the same common course of scientific education as the majority of his readers. Now that the mathematical interpretation of Faraday's conceptions

regarding the nature of electric and magnetic forces has been given by Clerk Maxwell, we see how great a degree of exactness and precision was really hidden behind the words, which to Faraday's contemporaries appeared either vague or obscure; and it is in the highest degree astonishing to see what a large number of general theorems, the methodical deduction of which requires the highest powers of mathematical analysis, he found by a kind of intuition, with the security of instinct, without the help of a single mathematical formula. I have no intention of blaming his contemporaries, for I confess that many times I have myself sat hopelessly looking upon some paragraph of Faraday's descriptions of lines of force, or of the galvanic current being an axis of power, &c. A single remarkable discovery may, of course, be the result of a happy accident, and may not indicate the possession of any special gift on the part of the discoverer; but it is against all rules of probability, that the train of thought which has led to such a series of surprising and unexpected discoveries, as were those of Faraday, should be without a firm, although perhaps hidden, foundation of truth. We must also in his case acquiesce in the fact that the greatest benefactors of mankind usually do not obtain a full reward during their lifetime, and that new ideas need the more time for gaining general assent the more really original they are, and the more power they have to change the broad path of human knowledge.

Faraday's electrical researches, although embracing a great number of apparently minute and disconnected questions, all of which he has treated with the same careful attention and conscientiousness, really always aim at two fundamental problems of natural philosophy, the one, more regarding the nature of the forces termed physical, or of forces working at a distance; the other, in the same way, regarding chemical forces, or those which act from molecule to molecule, and the relation between these and the first.

I shall give you only a short exposition on the degree of development which has been reached in the present state of science with regard to the first of these problems. The discussion of this question amongst scientific men is not yet finished, although, I think, it approaches its end. It is entangled with many geometrical and mechanical difficulties. How these are to be solved, and what are the arguments *pro* and *contra*, I cannot undertake to explain in a short public lecture, with any hope of gaining your scientific conviction. I can therefore give only a short statement of this side of the question, representing my own opinions; but I must not conceal the fact, that several men of great scientific merit, principally among my own countrymen, do not yet agree with me.

The great fundamental problem which Faraday called up anew for discussion was the existence of forces working directly at a distance

without any intervening medium. During the last and the beginning of the present century, the model, after the likeness of which nearly all physical theories had been formed, was the force of gravitation acting between the sun, the planets, and their satellites. It is known with how much caution and even reluctance, Sir Isaac Newton himself proposed his grand hypothesis, which was destined to become the first great and imposing example of the power of true scientific method. We need not wonder that Newton's successors attempted at first to gain the same success by introducing analogous assumptions into all the various branches of natural philosophy. Electrostatic and magnetic phenomena especially appeared as near relations to gravitation, because electric and magnetic attractions and repulsions, according to Coulomb's measurements, diminish in the same proportion as gravity with increasing distance.

But then came Oerstedt's discovery of the motions of magnets under the influence of electric currents. The force acting in these phenomena had a new and very singular character. It seemed as if this force would drive a single isolated pole of a magnet in a circle around the wire conducting the current, on and on, without end, never coming to rest. And although it is not possible really to separate one pole of a magnet from the other, Ampère succeeded in producing such continuous circular motions by making a part of the current itself moveable with the magnet.

This was the starting point for Faraday's researches on electricity. He saw that a motion of this kind could not be produced by any force of attraction or repulsion, working from point to point. The first motive which guided him seems to have been an instinctive foreboding of the law of conservation of energy, which many attentive observers of nature had entertained before it was brought by Joule to a precise scientific definition. If the current is able to increase the velocity of the magnet, the magnet must react on the current. So he made the experiment, and discovered induced currents. He traced them out through all the various conditions under which they ought to appear. He found that an electromotive force striving to produce these currents arises wherever and whenever magnetic force is generated or destroyed. He concluded that in a part of space traversed by magnetic force there ought to exist a peculiar state of tension, and that every change of this tension produces electromotive force. This unknown hypothetical state he called provisionally the electrotonic state, and he was occupied for years and years in finding out what this electrotonic state was. He first discovered in 1838 the dielectric polarisation of electric insulators subject to electric forces. Such bodies, under the influence of electric forces, exhibit phenomena perfectly analogous to those observed in soft iron under the influence

of the magnetic force. Eleven years later, in 1849, he was able to demonstrate that all ponderable matter is magnetised under the influence of sufficiently intense magnetic force, and at the same time he discovered the phenomena of diamagnetism, which indicated that even space, devoid of all ponderable matter, is magnetisable. The most simple explanation of these phenomena, indeed, is, that diamagnetic bodies are less magnetisable than a vacuous space, or than the luminiferous ether filling that space. In this way real changes corresponding to that hypothetical electrotonic state were demonstrated, and now, with quite a wonderful sagacity and intellectual precision, Faraday performed in his brain the work of a great mathematician without using a single mathematical formula. He saw with his mind's eye that magnetised and dielectric bodies ought to have a tendency to contract in the direction of the lines of force, and to dilate in all directions perpendicular to the former, and that by these systems of tensions and pressures in the space which surrounds electrified bodies, magnets or wires conducting electric currents, all the phenomena of electro-static, magnetic, electro-magnetic attraction, repulsion, and induction could be explained, without recurring at all to forces acting directly at a distance. This was the part of his path where so few could follow him; perhaps a Clerk Maxwell, a second man of the same power and independence of intellect, was needed to reconstruct in the normal methods of science the great building, the plan of which Faraday had conceived in his mind, and attempted to make visible to his contemporaries.

Nobody can deny that this new theory of electricity and magnetism, originated by Faraday and developed by Maxwell, is in itself well consistent, in perfect and exact harmony with all the known facts of experience, and does not contradict any one of the general axioms of dynamics, which have been hitherto considered as the fundamental truths of all natural science, because they have been found valid, without any exception, in all known processes of nature. A confirmation of great importance was given to this theory by the circumstance demonstrated by Clerk Maxwell, that the qualities which it must attribute to the imponderable medium filling space are able to produce and sustain magnetic and electric oscillations, propagating like waves, and with a velocity exactly equal to that of light. Several parts even of the theory of light are deduced with less difficulty from this new theory than from the well-known undulatory theory of Huyghens, which ascribes to the luminiferous ether the qualities of a rigid elastic body.

Nevertheless, the adherents of direct action at a distance have not yet ceased to search for solutions of the electromagnetic problem. The moving forces exerted upon each other by two wires conducting

galvanic currents had long ago been reduced in a very ingenious way by Ampère, to attracting or repelling forces belonging to the linear elements of every current. The intensity of these forces is considered to depend not only on the distance of both parts of the current, but also in a rather complicated manner on the angles which the directions of the two currents make with each other and with the straight line joining them both. Ampère was not acquainted with induced currents, but the phenomena of these could be derived from the law of Ampère, connecting it with the general law, deduced by Faraday from his experiments, that the current induced by the motion of a magnet or of another current always resists this motion. The general mathematical expression of this law was established by Professor Neumann, of Königsberg. It gave directly, not the value of the forces, but the value of their mechanical work, the value of what mathematicians call an electrodynamic potential, and it reduced electromagnetic phenomena to forces acting, not from point to point, but from one linear element of a current to another. Linear elements of a wire conducting a galvanic current are, of course, complicated structures compared with atoms. I have myself elaborated several mathematical papers to prove that this formula of Professor Neumann was in harmony with all the known phenomena exhibited by closed galvanic circuits, and that it did not come into contradiction with the general axioms of mechanics in any case of electric motion. I succeeded in finding an experimental method of observing electrostatic effects of electromagnetic induction under conditions in which closed circuits could not be generated. This experiment decided against the supposition that Neumann's theory was complete so long as only the electric motions in metallic or fluid conductors were considered as active currents, but it was in accordance with the theory of Faraday and Maxwell, who supposed that from the extremities of conducting bodies, where an electric charge collects, electric motion is continued through the insulating media separating them.

Other eminent men have tried to reduce electromagnetic phenomena to forces acting directly between distant quantities of the hypothetical electric fluids, with an intensity which depends not only on the distance, but also on the velocities and accelerations of those electric quantities. Such theories have been proposed by Professor W. Weber, of Göttingen, by Riemann, the too early-deceased mathematician, and by Professor Clausius, of Bonn. All these theories explain very satisfactorily the phenomena of closed galvanic currents. But applied to other electric motions, they all come into contradiction with the general axioms of dynamics.

The hypothesis of Professor Weber makes the equilibrium of electricity unstable in any conductor of moderate dimensions, and

renders possible the development of infinite quantities of work from finite bodies. I do not find that the objections, brought forward at first by Sir W. Thomson and Professor Tait in their Treatise on Natural Philosophy, and discussed and specialised afterwards by myself, have been invalidated by the discussions going on about this question. The hypothesis of Riemann, which he did not himself publish during his lifetime, labours under the same objection, and is at the same time in contradiction to Newton's axiom, which established the equality of action and reaction for all natural forces.

The hypothesis of Professor Clausius avoids the first objection, but not the second, and the author himself has conceded that this objection could be removed only by the assumption of a medium filling all space, between which and the electric fluids the forces acted.

The present development of science shows then, I think, a state of things very favourable to the hope that Faraday's fundamental conceptions may in the immediate future receive general assent. His theory, indeed, is the only one existing which is at the same time in perfect harmony with the facts as far as they are observed, and does not beyond the reach of facts lead into any contradiction of the general axioms of dynamics.

Clerk Maxwell himself has developed his theory only for closed conducting circuits. I have endeavoured during the last few years to investigate the results of this theory also for conductors not forming closed circuits. I can already say that the theory is in harmony with all the observations we have on the phenomena of open circuits: I mean (1) the oscillatory discharge of a condenser through a coil of wire, (2) my own experiments on electromagnetically induced charges on a rotating condenser, and (3) Mr. Rowland's observations on the electromagnetic effect of a rotatory disc charged with one kind of electricity.

The deciding assumption which removes the theoretical difficulties is that introduced by Faraday, who assumed that any electric motion in a conducting body which charges its surface with electricity is continued in the surrounding insulating medium as beginning or ending dielectric polarisation with an intensity equivalent to that of the current. A second inference from this supposition is, that the forces working at a distance do not exist, or are at least unimportant, when compared with the tensions and pressures of the dielectric medium.

It is not at all necessary to accept any definite opinion about the ultimate nature of the agent which we call electricity. Faraday himself avoided as much as possible giving any affirmative assertion regarding this problem, although he did not conceal his disinclination to believe in the existence of two opposite electric fluids.

For our own discussion of the electrochemical phenomena, to which we shall now turn, I beg permission to use the language of the old dualistic theory, which considers positive and negative electricity as two imponderable substances, because we shall have to speak principally on relations of quantity.

We shall try to imitate Faraday as well as we can by keeping carefully within the domain of phenomena, and, therefore, need not speculate about the real nature of that which we call a quantity of positive or negative electricity. Calling them substances of opposite sign, we imply with this name nothing else than the fact that a positive quantity never appears or vanishes without an equal negative quantity appearing or vanishing at the same time in the immediate neighbourhood. In this respect they behave really as if they were two substances, which cannot be either generated or destroyed, but which can be neutralised and become imperceptible by their union.

I see very well that this assumption of two imponderable fluids of opposite qualities is a rather complicated and artificial machinery, and that the mathematical language of Clerk Maxwell's theory expresses the laws of the phenomena very simply and very truly, with a much smaller amount of hypothetical implications; but I confess I should really be at a loss to explain without the use of mathematical formulæ, what he considers as a quantity of electricity, and why such a quantity is constant, like that of a substance. The original old notion of substance is not at all identical with that of matter. It signifies, indeed, that which behind the changing phenomena lasts as invariable, which can be neither generated nor destroyed, and in this oldest sense of the word we may really call the two electricities substances.

I prefer the dualistic theory, because it expresses clearly the perfect symmetry between the positive and negative side of electric phenomena, and I keep the well known supposition that as much negative electricity enters where positive goes away, because we are not acquainted with any phenomena which could be interpreted as corresponding with an increase or a diminution of the total electricity contained in any body. The unitary theory, which assumes the existence of only one imponderable electrical substance, and ascribes the effects of opposite kind to ponderable matter itself, affords a far less convenient basis for an electrochemical theory.

I now turn to the second fundamental problem aimed at by Faraday, the connection between electric and chemical force.

Already before Faraday went to work, an elaborate electrochemical theory had been established by the renowned Swedish chemist, Berzelius, which formed the connecting link of the great work of his life, the systematisation of the chemical knowledge of his time. His

starting point was the series in which Volta had arranged the metals according to the electric tension which they exhibit after contact with each other. Metals easily oxidised occupied the positive end of this series, those with small affinity for oxygen the negative end. Metals widely distant in the series develope stronger electric charges than those near to each other. A strong positive charge of one metal, and a strong negative of the other, must cause them to attract each other and to cling to each other. The same faculty of exciting each other electrically was ascribed by Berzelius to all the other elements; he arranged them all into a series, at the positive end of which he placed potassium, sodium, barium, calcium, &c.; at the negative end oxygen, chlorine, bromine, &c. Two atoms of different elements coming into contact are supposed to excite each other electrically, like the metals in Volta's experiment. Berzelius' conceptions about the distribution of opposite electricities in the molecules, and his deductions regarding the intensity of these forces, were not very clear, and not in harmony with the laws of electric forces which had already been developed by Green and Gauss. A fundamental point which Faraday's experiment contradicted was the supposition that the quantity of electricity collected in each atom was dependent on their mutual electrochemical differences, which Berzelius considered as the cause of their apparently greater chemical affinity.

His theory of the binary character of all chemical compounds was also connected with this electrochemical theory. Two elements, as he supposed, one positive, the other negative, could unite to a compound of the first degree, a basic oxide or an acid; two such compounds into a compound of the second degree, a salt. But there was nothing to prevent one atom of every positive element from uniting as directly with two, three, or even seven of another negative element as with one. The same was assumed by Berzelius for negative elements. The modern experience of chemistry directly contradicts these statements. But although the fundamental conceptions of Berzelius' theory have been forsaken, chemists have not ceased to speak of positive and negative constituents of a compound body. Nobody can overlook that such a contrast of qualities as was expressed in Berzelius' theory really exists, well developed at the extremities, less evident in the middle terms of the series, and playing an important part in all chemical actions, although often subordinated to other influences.

When Faraday began to study the phenomena of decomposition by the galvanic current, which of course were considered by Berzelius as amongst the firmest supports of his theory, he put a very simple question, the first question, indeed, which every chemist speculating about electrolysis ought to have thought of. He asked, what is the quantity of electrolytic decomposition if the same quantity of electricity is sent

through several electrolytic cells. By this investigation he discovered that most important law, generally known under his name, but called by him the law of definite electrolytic action.

When he began his experiments, neither Daniell's nor Grove's battery was known, and there were no means of producing currents of constant intensity; the methods of measuring this intensity were also in their infancy. This may excuse his predecessors. Faraday overcame this difficulty by sending the same current of electricity for the same time through a series of two or more electrolytic cells. He proved at first that the dimensions of the cell, and the size of the metallic plates through which the current entered and left the cell, had no visible influence upon the quantity of the products of decomposition. Cells containing the same electrolytic fluid between plates of the same metals gave always the same quantity, after being traversed by the same current. Then he compared the amount of decomposition in cells containing different electrolytes, and he found it exactly proportional to the chemical equivalents of the elements, which were either separated or converted into new compounds.

Faraday concluded from his experiments that a definite quantity of electricity cannot pass a voltametric cell containing acidulated water between electrodes of platinum, without setting free at the negative electrode a corresponding definite amount of hydrogen, and at the positive electrode the equivalent quantity of oxygen, one atom of oxygen for every pair of atoms of hydrogen. If instead of hydrogen any other element capable of replacing hydrogen is separated from the electrolyte, this is done also in a quantity exactly equivalent to the quantity of hydrogen which would have been evolved by the same electric current. According to the modern chemical theory of quantivalence, therefore, the same quantity of electricity passing through an electrolyte either sets free, or transfers to other combinations, always the same number of units of affinity at both electrodes; for instance,

instead of $\left.\begin{matrix}H\\H\end{matrix}\right\}$, either $\left.\begin{matrix}K\\K\end{matrix}\right\}$, or $\left.\begin{matrix}Na\\Na\end{matrix}\right\}$, or Ba}, or Ca}, or Zn},

or Cu} from cupric salts,

or $\left.\begin{matrix}Cu\\Cu\end{matrix}\right\}$ from cuprous salts, &c.

The simple or compound halogens separating at the other electrodes, are equivalent of course to the quantity of the metallic element with which they were formerly combined.

According to Berzelius' theoretical views, the quantity of electricity collected at the point of union of two atoms ought to increase with the strength of their affinity. Faraday demonstrated by experiment, that so far as this electricity came forth in electrolytic decomposition,

its quantity did not at all depend on the degree of affinity. This was really a fatal blow to Berzelius' theory.

Since that time our experimental methods and our knowledge of the laws of electrical phenomena have made enormous progress, and a great many obstacles have now been removed which entangled every one of Faraday's steps, and obliged him to fight with the confused ideas and ill-applied theoretical conceptions of some of his contemporaries. The original voltameter of Faraday, an instrument which measured the quantity of gases evolved by the decomposition of water, in order to determine with it the intensity of the galvanic current, has been replaced by the silver voltameter of Poggendorff, which permits of much more exact determinations by the quantity of silver deposited from a solution of silver nitrate on a strip of platinum. We have galvanometers which not only indicate that there is a galvanic current, but likewise measure its electromagnetic intensity very exactly and in a very short time, and do this as well for the highest as for the lowest degrees of intensity. We have electrometers, like the quadrant electrometer of Sir W. Thomson, able to measure differences of electric potential corresponding to less than one-hundredth of a Daniell's cell. As for the frequently-used term of electric potential, a term introduced by Green, you may translate it as signifying the electric pressure to which the positive unit of electricity is subject at a certain place. We need not hesitate to say that the more experimental methods were refined, the more completely were the exactness and generality of Faraday's law confirmed.

In the beginning Berzelius and the adherents of Volta's original theory of galvanism, based on the effects of metallic contact, raised many objections against Faraday's law.

By the combination of Nobili's astatic pairs of magnetic needles with Schweigger's multiplier, a coil of copper wire with numerous circumvolutions, galvanometers became so delicate that they were able to indicate the electrochemical equivalent of currents so feeble as to be quite imperceptible by all chemical methods. With the newest galvanometers you can very well observe currents which would require to last a century before decomposing one milligram of water, the smallest quantity that is usually weighed on chemical balances. You see that if such a current lasts only some seconds or some minutes, there is not the slightest hope of discovering its products of decomposition by chemical analysis. And even if it should last a long time, the minute quantities of hydrogen collected at the negative electrode may vanish, because they combine with the traces of atmospheric oxygen absorbed by the liquid. Under such conditions a feeble current may continue as long as you like without producing any visible trace of electrolysis, not even of galvanic polarisation, the appearance of which can be used as

an indication of previous electrolysis. Galvanic polarisation, as you know, is an altered state of the metallic plates which have been used as electrodes during the decomposition of an electrolyte. Polarised electrodes, when connected by a galvanometer, give a current which they did not give before being polarised. By this current the plates are discharged again and returned to their original state of equality. The most probable explanation of this polarisation is that molecules of the electrolyte, charged with electricity, are carried by the current to the surface of the metal, itself charged with opposite electricity, and are retained there by electric attraction. That really constituent atoms of the electrolyte partake in the production of galvanic polarisation cannot well be doubted, because this state can be produced and also destroyed purely by chemical means. If hydrogen has been carried to an electrode by the current, contact with the atmospheric oxygen removes the state of polarisation.

The depolarising current is indeed a most delicate means of discovering previous decomposition. But even this may fail if the nascent polarisation is destroyed by an intervening chemical action, like that of the oxygen of the air. To avoid this, delicate experiments on this subject cannot be performed except in vessels carefully purified of all gases.

I have lately succeeded in doing this in a far more perfect way than before, by using the hermetically sealed cell (Fig. 1), which contains

FIG. 1.

water acidulated with sulphuric acid. Two platinum wires, *b* and *c*, and a third platinum wire, *a*, which in the interior is connected with a spiral of palladium, can be used as electrodes. The tube, before it had been closed, was connected with a water-pump, and at the same time oxygen was evolved from *b* and *c* by two Grove's elements; the hydrogen carried to the palladium wire, *a*, was occluded in the metal. In this way the liquid in the tube is washed out with oxygen under low pressure and freed from all other gases. After the closing of the tube, the remaining small traces of electrolytic oxygen combine slowly with the hydrogen of the palladium. Traces of hydrogen occluded in the platinum wires *b* and *c* can be transferred by a feeble electromotive force into the palladium; and even new quantities of electrolytic gases, evolved after closing the tube, can be removed again by a Daniell's cell, which carries hydrogen to the palladium, where it is occluded, and oxygen to *b* and *c*, where it combines with hydrogen, as long as traces of this gas are dissolved in the liquid. The rest of the oxygen absorbed by the liquid combines with the occluded hydrogen.

I have ascertained with this apparatus that under favourable conditions one can observe the polarisation produced during a few seconds by a current which would decompose only one milligram of water in a century.

But even if the appearance of galvanic polarisation should not be acknowledged by opponents as a sufficient indication of previous decomposition, it is not difficult at present to reduce the indications of a good galvanometer to absolute measure, and to calculate the amount of decomposition which ought to be expected according to Faraday's law, and to verify that in all the cases in which no products of electrolysis can be discovered, their amount is too small for chemical analysis.

Products of decomposition cannot appear at the electrodes without the occcurrence of motions of the constituent molecules of the electrolyte throughout the whole length of the liquid. On this point the majority of Faraday's predecessors were already agreed, but they differed from each other as soon as they came to the question what those motions were. Faraday saw very clearly the importance of this problem, and again appealed to experiment. He filled two cells with an electrolytic fluid, connecting them by a thread of asbestos wetted with the same fluid, in order to determine separately the quantity of all the chemical constituents transferred to the one and the other extremity of the electrolytic conductor. You know that he proposed for these atoms or groups of atoms transported by the current through the fluid the Greek word "Ions," the "Travellers;" and comparing the current of positive electricity with a stream of water, he called "cations" those

atoms which went down the stream in the same direction with the positive electricity to the cathode, the metallic plate through which this electricity left the fluid. The "anions," on the contrary, go up the stream to the anode, the metal plate which is the source of the current of + E. Cations generally are atoms which are substitutes of hydrogen; anions are halogens.

This subject has been studied very carefully and for a great number of liquids, by Professor Hittorff, of Münster, and Professor G. Wiedemann, of Leipsic. They found that generally the velocity of the cation and the anion is different. Professor F. Kohlrausch, of Würzburg, has brought to light the very important fact that in diluted solutions of salts, including hydrates of acids and hydrates of caustic alkalis, every ion under the influence of currents of the same density moves on with its own peculiar velocity, independently of other ions moving at the same time in the same or in opposite directions.

Among the cations hydrogen has the greatest velocity, then follow potassium, ammonium, silver, sodium, afterwards the bivalent atoms of barium, copper, strontium, calcium, magnesium, zinc; near to the latter appears univalent lithium. Among the anions hydroxyl (OH) is the first, then follow the other univalent atoms iodine, bromine, cyanogen, chlorine, the compounds NO_3, ClO_3, the bivalent halogens of sulphuric and carbonic acid; after these fluorine and the halogen of acetic acid ($C_2H_3O_2$). The only exception to this rule is the difference observed between the decomposition of univalent and bivalent compounds. Generally the velocity of any ion when separated from a bivalent mate is less than when separated from one or two univalent mates.

It seems possible that the majority of molecules SO_4H_2 may be divided electrolytically into SO_4 and H_2, some of them on the other hand into SO_4H and H. By the latter some hydrogen would be carried backwards, and therefore the velocity of the total amount might appear diminished.

If both ions are moving, we shall find liberated at each electrode (1) that part of the corresponding ion which has been newly carried to that side: (2) another part which has been left by the opposite ion, with which it had been formerly combined. The total amount of chemical motion in every section of the fluid is, therefore, represented by the sum of the equivalents of the cation gone forwards, and of the anion gone backwards, in the same way as in the dualistic theory of electricity the total amount of electricity flowing through a section of the conductor corresponds to the sum of positive electricity going forwards and of negative electricity going backwards.

This established, Faraday's law tells us that through each section of an electrolytic conductor we have always equivalent electrical and chemical motion. The same definite quantity of either positive or

negative electricity moves always with each univalent ion, or with every unit of affinity of a multivalent ion, and accompanies it during all its motions through the interior of the electrolytic fluid. This quantity we may call the electric charge of the atom.

I beg to remark that hitherto we have spoken only of phenomena. The motion of electricity can be observed and measured. Independently of this, the motion of the chemical constituents can also be measured. Equivalents of chemical elements and equivalent quantities of electricity are numbers which express real relations of natural objects and actions. That the equivalent relation of chemical elements depends on the pre-existence of atoms may be hypothetical; but we have not yet any theory sufficiently developed which can explain all the facts of chemistry as simply and as consistently as the atomic theory developed in modern chemistry.

Now the most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long as it moves about on the electrolytic liquid, each ion remains united with its electric equivalent or equivalents. At the surface of the electrodes decomposition can take place if there is sufficient electromotive force, and then the ions give off their electric charges and become electrically neutral.

The same atom can be charged in different compounds with equivalents of positive or of negative electricity. Faraday pointed out sulphur as being an element which can act either as anion or as cation. It is anion in sulphide of silver, a cation perhaps in strong sulphuric acid. Afterwards he suspected that the deposition of sulphur from sulphuric acid might be a secondary result. The cation may be hydrogen, which combines with the oxygen of the acid, and drives out the sulphur. But if this is the case, hydrogen recombined with oxygen to form water must retain its positive charge, and it is the sulphur, which in our case must give off positive equivalents to the cathode. Therefore this sulphur of sulphuric acid must be charged with positive equivalents of electricity. The same may be applied to a great many other instances. Any atom or group of atoms which can be substituted by secondary decomposition for an ion must be capable of giving off the corresponding equivalent of electricity.

When the positively charged atoms of hydrogen or any other cation are liberated from their combination and evolved as gas, the gas becomes electrically neutral; that is, according to the language of the dualistic theory, it contains equal quantities of positive and negative electricity; either every single atom is electrically neutralised, or one atom, remaining positive, combines with another charged negatively.

This latter assumption agrees with the inference from Avogadro's law, that the molecule of free hydrogen is really composed of two atoms.

Now arises the question: Are all these relations between electricity and chemical combination limited to that class of bodies which we know as electrolytes. In order to produce a current of sufficient strength to collect enough of the products of decomposition without producing too much heat in the electrolyte, the substance which we try to decompose ought not to offer too much resistance to the current. But this resistance may be very great, and the motion of the ions may be very slow, so slow indeed that we should need to allow it to go on for hundreds of years before we should be able to collect even traces of the products of decomposition; nevertheless all the essential attributes of the process of electrolysis could subsist. In fact we find the most various degrees of conducting power in various liquids. For a great number of them, down to distilled water and pure alcohol, we can observe the passage of the current with a sensitive galvanometer. But if we turn to oil of turpentine, benzene, and similar substances, the galvanometer becomes silent. Nevertheless these fluids also are not without a certain degree of conducting power. If you connect an electrified conductor with one of the electrodes of a cell filled with oil of turpentine, the other with the earth, you will find that the electricity of the conductor is discharged unmistakably more rapidly through the oil of turpentine than if you take it away and fill the cell only with air.

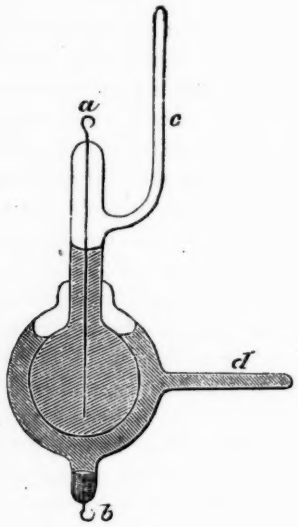
We may in this case also observe polarisation of the electrodes as a symptom of previous electrolysis. Connect the two pieces of platinum in oil of turpentine with a battery of eight Daniells, let it stay 24 hours, then take away the battery, and connect the electrodes with a quadrant electrometer; it will indicate that the two surfaces of platinum, which were homogeneous before, produce an electromotive force which deflects the needle of the electrometer. The electromotive force of this polarisation has been determined in some instances by Mr. Picker in the Laboratory of the University of Berlin; he has found that the polarisation of alcohol decreases with the proportion of water which it contains, and that that of the purest alcohol, ether, and oil of turpentine, is about 0·3, that of benzene 0·8 of a Daniell's element.

Another sign of electrolytic conduction is, that liquids placed between two different metals produce an electromotive force. This is never done by metals of equal temperature, or by other conductors which, like metals, let electricity pass without being decomposed. The production of an electromotive force is observed even with a great many rigid bodies, although very few of them allow us to observe electrolytic conduction with the galvanometer, and even these

only at temperatures near their melting points. I remind you of the galvanic pile of Zamboni, in which pieces of dry paper are intercalated between thin leaves of metal. If the connection lasts long enough, even glass, resin, shellac, paraffin, sulphur—the best insulators we know—do the same. It is nearly impossible to prevent the quadrants of a delicate electrometer from being charged by the insulating bodies by which they are supported.

In all the cases which I have quoted, one might suspect that traces of humidity absorbed by the substance or adhering to their surface were the electrolytes. I show you, therefore, this little Daniell's cell, Fig. 2, constructed by my former assistant, Dr. Giese, in which a solu-

Fig. 2.



tion of sulphate of copper with a platinum wire, *a*, as an electrode, is enclosed in a bulb of glass hermetically sealed. This is surrounded by a second cavity, sealed in the same way, which contains a solution of zinc sulphate and some amalgam of zinc, to which a second platinum wire, *b*, enters through the glass. The tubes *c* and *d* have served to introduce the liquids, and have been sealed afterwards. It is, therefore, like a Daniell's cell, in which the porous septum has been replaced by a thin stratum of glass. Externally all is symmetrical at the two poles; there is nothing in contact with the air but a closed surface of glass, through which two wires of platinum penetrate. The whole

charges the electrometer exactly like a Daniell's cell of very great resistance, and this it would not do if the septum of glass did not behave like an electrolyte: for a metallic conductor would completely destroy the action of the cell by its polarisation.

All these facts show that electrolytic conduction is not at all limited to solutions of acids or salts. It will, however, be rather a difficult problem to find out how far the electrolytic conduction is extended, and I am not yet prepared to give a positive answer. What I intended to remind you of was only that the faculty to be decomposed by electric motion is not necessarily connected with a small resistance to the current. It is easier for us to study the cases of small resistance, but the illustration which they give us about the connection of electric and chemical force is not at all limited to the acid and saline solutions usually employed.

Hitherto we have studied the motions of ponderable matter as well as of electricity, going on in an electrolyte. Let us now study the forces which are able to produce these motions. It has always appeared somewhat startling to everybody who knows the mighty power of chemical forces, and the enormous quantity of heat and mechanical work which they are able to produce, how exceedingly small is the electric attraction at the poles of a battery of two Daniell's cells, which nevertheless is able to decompose water. 1 gram of water, produced by burning hydrogen with oxygen, developes so much heat, that this heat transformed by a steam engine into mechanical work would raise the same weight to a height of 1,600,000 metres. And on the contrary we require to use the most delicate contrivances to show that a gold leaf or a little piece of aluminium hanging on a silk fibre can be at all moved by the electric attraction of the battery. The solution of this riddle is found if we look at the quantities of electricity with which the atoms appear to be charged.

The quantity of electricity which can be conveyed by a very small quantity of hydrogen, when measured by its electrostatic forces, is exceedingly great. Faraday saw this, and endeavoured in various ways to give at least an approximate determination. He ascertained that even the most powerful batteries of Leyden jars, discharged through a voltameter, give scarcely any visible traces of gases. At present we can give definite numbers. The electrochemical equivalent of the electromagnetic unit of the galvanic current has been determined by Bunsen, and more recently by other physicists. This determination was followed by the very difficult comparison of the electromagnetic and electrostatic effects of electricity, accomplished at first by Professor W. Weber, and afterwards under the auspices of the British Association by Professor Clerk Maxwell.* The result is,

* According to the latest and most careful measurements of the electrochemical

that the electricity of 1 mgrm. of water, separated and communicated to two balls, 1 kilomt. distant, would produce an attraction between them equal to the weight of 26,800 kilogr.

As I have already remarked, the law that the intensity of t force is inversely proportional to the square of the distance, and directly proportional to the quantities of attracting and of attracted mass, holds good as well in the case of gravitation as in that of electric attraction and repulsion. We may, therefore, compare the gravitation acting between two quantities of hydrogen and oxygen with the attraction of their electric charges. The result will be independent of the size and the distance of these quantities. We find that the electric force is as great as the gravitation of ponderable masses, being 71,000 billion times greater than that of the oxygen and hydrogen* containing these electric charges.

effect, performed by Professor Kohlrausch, junr., the electromagnetic unit of the galvanic current, as it was defined by W. Weber (= 0·1 of the British Association unit), decomposes 0·009476 mgrm. of water per second. This same unit-current of Weber transfers about $300 \cdot 10^9$ electrostatic units of electricity (Weber himself gave $311 \cdot 10^9$, Maxwell $288 \cdot 10^9$) through each section of the circuit per second, half of them being positive, half of them negative, the two halves going in opposite directions. The electrostatic unit introduced by Gauss and W. Weber is that quantity of electricity which repels the same quantity at the distance of one millimeter with unit force, that is, with a force which, acting during one second upon one milligram, transmits to it a velocity of one millimeter per second. Gravity acting upon one milligram produces an acceleration 9,809 times as great. Weber's unit force, therefore, is equal to $\frac{1}{9809}$ of the weight of one milligram.

The force, F, measured by weight, with which the electric quantity, + E, measured in electrostatic units, attracts the opposite quantity − E, at a distance r is equal to—

$$F = \frac{E^2}{r^2} \cdot \frac{1}{9809} \text{ mgrm.}$$

If E is the quantity carried to each electrode during the decomposition of one milligram of water, it is according to the determinations quoted before $= 1618 \cdot 10^{10}$ units, and if we put r = 1 kilometer = 1,000,000 millimeters, we get the result quoted above.

* The gravity of a weight m is the force of attraction between it and the mass of the earth, which may be considered as concentrated in the central point of the earth. If h is the mean density of the earth, and r its radius, the mass of the earth will be—

$$\frac{4\pi}{3} r^3 . h.$$

If G is the force of attraction between two units of mass at unit of distance, the attraction of the mass m by the earth will be—

$$gm = \frac{4\pi}{3} rh . Gm.$$

Take—

$$\frac{\pi}{2} r = 10^7 \text{ meters} = 10^{10} \text{ mm.}$$

$$h = 5 \cdot 62 \text{ mgrms. per cub. mm.,}$$

The total force exerted by the attraction of an electrified body upon another charged with opposite electricity is always proportional to the quantity of electricity contained on the attracting as on the attracted body.

Although, therefore, the attracting forces exerted by the poles of a little battery able to decompose water on such electric charges as we can produce with our electric machines, are very moderate, the forces exerted by the same little apparatus on the enormous charges of the atoms in one milligram of water may very well compete with the mightiest chemical affinity.

If we now turn to investigate how the motions of the ponderable molecules are dependent upon the action of these forces, we must distinguish two different cases. At first we may ask what forces are wanted to call forth motions of the ions with their charge through the interior of the fluid; secondly, what are wanted to separate the ion from the fluid and its previous combinations?

Let us begin with the case in which the conducting liquid is surrounded everywhere by insulating bodies. Then no electricity can enter, none can go out through its surface, but positive electricity can be driven to one side, negative to the other, by the attracting and repelling forces of external electrified bodies. This process going on as well in every metallic conductor is called "electrostatic induction." Liquid conductors behave quite like metals under these conditions. Great quantities of electricities are collected, if large parts of the surfaces of the two bodies are very near to each other. Such an arrangement is called an electric condenser. We can arrange electric condensers in which one of the surfaces is that of a liquid, as Messrs. Ayrton and Perry have done lately. The water-dropping collector of electricity, invented by Sir W. Thomson, is a peculiar form of such a condenser, which can be charged with perfect regularity by the slightest electromotive force perceptible only to the most sensitive electrometer.

the attraction between $\frac{8}{9}$ mgrm. of oxygen and $\frac{1}{9}$ mgrm. of hydrogen contained in 1 mgrm. ofwater, and separated by a distance of 1 mm. will be—

$$\frac{1}{9} \cdot \frac{8}{9} \cdot G = \frac{g}{27{\cdot}5,62{\cdot}10^{10}},$$

or equal to the weight of—

$$\frac{65904}{10^{17}} \text{ mgrm.}$$

The attraction of the electric charges, which has been calculated before for a distance of 1 kilometer, reduced to that of 1 mm., will be equal to the weight of—

$$20800{\cdot}10^{18} \text{ mgrms.}$$

From this it follows that the attraction by gravitation of those two masses would become equal to the attraction of their electric charges, if each of the masses could be increased 71,300 billions of times.

Professor Wüllner has proved that even our best insulators, exposed to electric forces for a long time, are ultimately charged quite in the same way as metals would be charged in an instant. There can be no doubt that even electromotive forces less than $\frac{1}{100}$ Daniell produce perfect electrical equilibrium in the interior of an electrolytic liquid.

Another somewhat modified instance of the same effect is afforded by a voltametric cell containing two electrodes of platinum, which are connected with a Daniell's cell the electromotive force of which is insufficient to decompose the electrolyte. Under this condition the ions carried to the electrodes cannot give off their electric charges. The whole apparatus behaves, as was first accentuated by Sir W. Thomson, like a condenser of enormous capacity. The quantity of electricity, indeed, collected in a condenser under the same electromotive force is inversely proportional to the distance of the plates. If this is diminished to $\frac{1}{100}$, the condenser takes in 100 times as much electricity as before. Now, bringing the two surfaces of platinum and of the liquid into immediate contact, we reduce their interval to molecular distances. The capacity of such a condenser has been measured by Messrs. Varley, Kohlrausch, and Colley. I have myself made some determinations which show that oxygen absorbed in the fluid is of great influence on the apparent value. By removing all traces of gas I have got a value a little smaller than that of Kohlrausch, which shows that if we divide equally the total value of the polarisation between two platinum plates of equal size, the distance between the two strata of positive and negative electricity, the one lying on the last molecules of the metal, the other on those of the fluid, ought to be a ten millionth part (Kohlrausch $\frac{1}{10000000}$) of a millimeter. We always come nearly to the same limit, when we calculate the distances through which molecular forces are able to act, as already shown in several other instances by Sir W. Thomson.

Owing to the enormous capacity of such an electrolytic condenser, the quantity of electricity which enters into it, if it is charged even by a feeble electromotive force, is sufficiently great to be indicated easily by a galvanometer. What I now call charging the condenser, I have before called polarising the metallic plate. Both, indeed, are the same process, because electric motion is always accompanied in the electrolytes by chemical decomposition.

Observing the polarising and depolarising currents in a cell like that represented in Fig. 1, we can observe these phenomena with the most feeble electromotive forces of $\frac{1}{1000}$ Daniell, and I found that down to this limit the quantity of electricity entering into the condenser was proportional to the electromotive force by which it was collected. By taking larger surfaces of platinum, I suppose it will be possible to reach a limit much lower than that. If any chemical force existed besides that

of the electrical charges which could bind all the pairs of opposite ions together, and required any amount of work to be vanquished, an inferior limit ought to exist to such electromotive forces as are able to attract the ions to the electrodes, and to charge these as condensers. No phenomenon indicating such a limit has as yet been discovered, and we must, therefore, conclude that no other force resists the motions of the ions through the interior of the liquid than the mutual attractions of their electric charges. These are able to prevent the atoms of the same kind which repel each other from collecting at one place, and atoms of the other kind attracted by the former from collecting at any other part of the fluid, as long as no external electric force favours such distribution. The electric attraction, therefore, is able to produce an equal distribution of the opposite constituent atoms throughout the liquid, so that all parts of it are neutralised electrically as well as chemically.

On the contrary, as soon as an ion is to be separated from its electrical charge, we find that the electrical forces of the battery meet with a powerful resistance, the overpowering of which requires a good deal of work to be done. Usually the ions, losing their electric charges, are at the same time separated from the liquid; some of them are evolved as gases, others are deposited as rigid strata on the surface of the electrodes, like galvanoplastic copper. But the union of two constituents having powerful affinity to form a chemical compound, always produces, as you know very well, a great amount of heat, and heat is equivalent to work. On the contrary, decomposition of the compound substance requires work, because it restores the energy of the chemical forces which has been spent by the act of combination. Oxygen and hydrogen separated from each other contain a store of energy, for on burning the hydrogen in the oxygen they unite, form water, and develope a great amount of heat. In the water the two elements are contained, and their chemical attraction continues to work as before, keeps them firmly united, but can no more produce any change, any positive action. We must reduce the combined elements into their first state, we must separate them, applying a force which is capable of vanquishing their affinity before they are ready to renew their first activity. The amount of heat produced by the chemical combination is the equivalent of the work done by the chemical forces brought into action. It requires the same amount of work to separate the compound and to restore hydrogen and oxygen uncombined. I have already given the value of this amount calculated as a weight raised against the force of gravity.

Metals uniting with oxygen or halogens produce heat in the same way, some of them, like potassium, sodium, and zinc, even more than an equivalent quantity of hydrogen; less oxidisable metals, like copper,

silver and platinum, less. We find, therefore, that heat is generated when zinc drives copper out of its combination with the compound halogen of sulphuric acid, as is the case in a Daniell's cell.

If a galvanic current passes through any conductor, a metallic wire, or an electrolytic fluid, it evolves heat. Dr. Joule was the first who proved experimentally that if no other work is done by the current, the total amount of heat evolved in a galvanic circuit during a certain time is exactly equal to that which ought to have been generated by the chemical actions which have been performed during that time. But this heat is not evolved at the surface of the electrodes where these chemical actions take place, but is evolved in all the parts of the circuit, proportionally to the galvanic resistance of every part. From this it is evident that the heat evolved is an immediate effect, not of the chemical action, but of the galvanic current, and that the chemical work of the battery has been spent to produce only the electric action.

To keep up an electric current through an electric conductor, indeed, requires work to be done. New stores of positive electricity must be continually introduced at the positive end of the conductor, the repulsive force acting upon them having to be overcome; negative electricity, in the same way, into the negative end. This can be done by mere mechanical force, with an electric machine working by friction, or by electrostatic or by electromagnetic induction. In a galvanic current it is done by chemical force, but the work required remains the same.

If we apply Faraday's law, a definite amount of electricity passing through the circuit corresponds with a definite amount of chemical decomposition going on in every electrolytic cell of the same circuit. According to the theory of electricity, the work done by such a definite quantity of electricity which passes, producing a current, is proportionate to the electromotive force acting between both ends of the conductor. You see, therefore, that the electromotive force of a galvanic circuit must be, and is indeed, proportional to the heat generated by the sum of all the chemical actions going on in all the electrolytic cells during the passage of the same quantity of electricity. In the cells of the galvanic battery chemical forces are brought into action able to produce work; in cells in which decomposition is occurring, work must be done against opposing chemical forces; the rest of the work done appears as heat evolved by the current, as far as it is not used up to produce motions of magnets or other equivalents of work.

You see the law of the conservation of energy requires that the electromotive force of every cell must correspond exactly with the total amount of chemical forces brought into play, not only the mutual affinities of the ions, but also those minor molecular attractions pro-

duced by the water and other constituents of the fluid. These minor attractions have lately formed the subject of most valuable and extended calorimetric researches by Messrs. Andrews, Thomsen, and Berthelot. But even influences too minute to be measured by calorimetric methods may be discovered by measuring the electromotive force. I have myself deduced from the mechanical theory of heat the influence which the quantity of water contained in a solution of metallic salts has on the electromotive force. The chemical attraction between salt and water can be measured in this instance by the diminution of the tension of the aqueous vapours over the liquid, and the results of the theoretical deduction have been confirmed in a very satisfactory manner by the observations of Dr. James Moser.

Hitherto we have supposed that the ion with its electric charge is separated from the fluid. But the ponderable atoms can give off their electricity to the electrode, and remain in the liquid, being now electrically neutral. This makes scarcely any difference in the value of the electromotive force. For instance, if chlorine is separated at the anode, it will at first remain absorbed by the liquid; if the solution becomes saturated, or if we make a vacuum over the liquid, the gas will rise in bubbles. The electromotive force remains unaltered. The same may be observed with all the other gases. You see in this case that the change of electrically negative chlorine into neutral chlorine is the process which requires so great an amount of work, even if the ponderable matter of the atoms remains where it was.

On the contrary, if the electric attraction does not suffice to deprive the ions collecting at the surface of the electrodes of their electric charge, you will find the cation attracted and retained by the cathode, the anion by the anode, with a force far too great to be overpowered by the expansive force of gases. You may make a vacuum as perfect as you like over a cathode polarised with hydrogen, or an anode polarised with oxygen; you will not obtain the smallest bubble of gas. Increase the electric potential of the electrodes, so that the electric force becomes powerful enough to draw the electric charge of the ions over to the electrode: the ions will be liberated and free to leave the electrode, passing into the gaseous state or spreading in the liquid by diffusion. One cannot assume, therefore, that their ponderable matter is attracted by the electrode; if this were the case, this attraction ought to last after discharge as before. We must conclude, therefore, that the ions are drawn to the electrode only because they are charged electrically.

The more the surface of the positive electrode is covered with negative atoms of the anion, and the negative with the positive ones of the cation, the more is the attracting force of the electrodes exerted upon the ions of the liquid diminished by this second stratum of opposite

electricity covering them. On the contrary, the force with which the positive electricity of an atom of hydrogen situated at the surface of the electrode itself is attracted towards the negatively charged metal increases in proportion as more negative electricity collects before it on the metal, and behind it in the fluid.

The electrical force acting on equal quantities of electricity situated at the inside of one of the electric strata of a condenser is proportional to the electromotive force which has charged the condenser, and inversely proportional to the distance of the charged surfaces. If these are $\frac{1}{100}$ mm. apart, it is 100 times as great as if they are one millimeter apart. If we come, therefore, to molecular distances, like those calculated from the measurement of the capacity of polarised electrodes, the force is ten million times as great, and becomes able, even with a moderate electromotive force, to compete with the powerful chemical forces which combine every atom with its electric charge, and hold the atoms bound to the liquid.

Such is the mechanism by which electric force is concentrated at the surface of the electrodes and increased in its intensity to such a degree that it becomes able to overpower the mightiest chemical affinities we know of. If this can be done by a polarised surface, acting like a condenser charged by a very moderate electromotive force, can the attractions between the enormous electric charges of anions and cations be an unimportant and indifferent part of chemical affinity?

In a decomposing cell the ions resist external forces striving to separate them from their electric charges. Let the current go in the opposite direction, and you will have an opposite effect. In a Daniell's cell neutral zinc enters as cation into the electrolyte, taking with it only positive electricity, and leaving its negative electricity to the metallic plate. At the copper electrode positive copper separates from the electrolyte and is neutralised, giving off its charge to the electrode. But the Daniell's cell in which this goes on does work, as we have seen. We must conclude, therefore, that an equivalent of positive electricity, on charging an atom of zinc, does more work than the same equivalent does on charging an atom of copper.

You see, therefore, if we use the language of the dualistic theory and treat positive and negative electricities as two substances, the phenomena are the same as if equivalents of positive and negative electricity were attracted by different atoms, and perhaps also by the different values of affinity belonging to the same atom with different force. Potassium, sodium, zinc, must have strong attraction to a positive charge; oxygen, chlorine, bromine to a negative charge.

Do we perceive effects of such an attraction in other cases? Here we come to the much discussed question of Volta's assumption that electricity is produced by contact of two metals. About the fact there

can be no doubt. If we produce metallic contact between a piece of copper and a piece of zinc, opposed to each other like the two plates of a condenser, and carried by isolating rods of shell-lac we find that after contact the zinc is charged positively, the copper negatively. This is just the effect we ought to expect if zinc has a higher attracting force to positive electricity, this force working only through molecular distances. I have proposed this explanation of Volta's experiments in my little pamphlet on the "Conservation of Energy," published in 1847. All the facts observed with different combinations of metallic conductors are perfectly in harmony with it. Volta's law of the series of tension comprising all metallic conductors is easily deduced from it. If only metals come into play, their galvanic attractions produce instantaneously a state of electric equilibrium, so that no lasting current can occur. Electrolytic conductors, on the contrary, are decomposed chemically by every motion of electricity through their surface. Electric equilibrium, therefore, will not be possible before this decomposition has been finished, and till that stage is reached, the electric motion must continue. This point has been accentuated already by Faraday, as the essential difference between the two classes of conductors.

The original theory of Volta was incomplete in an essential point, because he was not acquainted with the fact of electrolytic decomposition. His original conception of the force of contact is, therefore, in contradiction to the law of Conservation of Energy; and even before this law was established and enunciated with scientific precision, there were many chemists and physicists, amongst them Faraday, who had the right instinct that this could not be the true explanation. The opponents of Volta's opinions tried to give chemical explanations also of those experiments of his, which were carried out exclusively with metal conductors. They might be oxidised by the oxygen of the air, and the amount of oxidation required for a very slight electric charge was so infinitesimal, that no chemical analysis could ever discover it; so small, that even in the highest vacuum, and in the purest specimens of hydrogen or nitrogen with which we might surround the plates, there was oxygen enough to continue the effect for years. From this point of view the chemical theory cannot be refuted. On the contrary, the so-called chemical theory of Volta's fundamental experiments was rather indefinite; it scarcely did more than tell us: here is the possibility of a chemical process, here electricity can be produced. But which kind, how much, to which potential, remained indefinite. I have not found in all the papers which have been written for the defence of the chemical theory, a clear explanation why zinc opposed to copper in liquids, where zinc really is oxidized and dissolved, becomes negative, and why in air and other gases it becomes positive, if the same cause,

namely oxidation, is at work. The hypothesis, on the contrary, of a different degree of affinity between the metals and the two electricities, gives a perfectly definite answer. I do not see why an actual chemical process should be wanted to charge the zinc and copper on contact. But you see that the forces, which according to their hypothesis produce the electric effect, are the same as those which must be considered as the cause of a main part of all chemical actions.

Again, the electric charges produced by contact of zinc and copper are very feeble. They have become measurable only with the help of the latest improvements introduced into the construction of electrometers by Sir W. Thomson; but the cause of their feeble intensity is evident. If you bring into narrow contact two plain and well-polished plates of zinc and copper, the quantity of electricity collected at both sides of their common surface is probably very great; but you cannot observe it before having separated the plates. Now it is impossible to separate them at the same instant over the whole extent of their surface. The charge which they retain will correspond with the inclined position which they have at the moment when the last point of contact is broken; then all the other parts of the surfaces are already at a distance from each other infinitely greater than molecular distance, and conduction in metals always establishes nearly instantaneously the electric equilibrium corresponding to the actual situation. If you wish to avoid this discharge during the separation of the plates, one of them must be isolated; then indeed we get a far more striking series of phenomena, those belonging to electricity of friction. Friction, probably, is only the means of producing a very close contact between the two bodies. If the surfaces are very clean and free from air, as for instance in a Geissler's tube, the slightest rolling contact is sufficient to develop the electric charge. I can show you two such tubes exhausted so far that very high electric tension is necessary to make the vacuum luminous, one containing a small quantity of mercury, the other the fluid compound of potassium and sodium. In the first the negative metal is intensely negative relatively to glass, in the second the metal is on the positive extremity of Volta's series; the glass proves to be more positive also in this case, but the difference is much smaller than with mercury, and the charge is feeble.

Faraday very often recurs to this to express his conviction that the forces termed chemical affinity and electricity are one and the same. I have endeavoured to give you a survey of the facts connected with the question, and to avoid as far as possible the introduction of hypotheses, except the atomic theory of modern chemistry. I think the facts leave no doubt that the very mightiest among the chemical forces are of electric origin. The atoms cling to their electric charges, and opposite electric charges cling to each other; but I do not suppose

that other molecular forces are excluded, working directly from atom to atom. Several of our leading chemists have lately begun to distinguish two classes of compounds, viz., molecular aggregates and typical compounds, the latter being united by atomic affinities, the former not.

Electrolytes belong to the latter class. If we conclude from the facts that every unit of affinity is charged with one equivalent either of positive or of negative electricity, they can form compounds, being electrically neutral only if every unit charged positively unites under the influence of a mighty electric attraction with another unit charged negatively. You see that this ought to produce compounds in which every unit of affinity of every atom is connected with one and only one other unit of another atom. This, as you will see immediately, is the modern chemical theory of quantivalence, comprising all the saturated compounds. The fact that even elementary substances, with few exceptions, have molecules composed of two atoms, makes it probable that even in these cases electric neutralisation is produced by the combination of two atoms, each charged with its full electric equivalent, not by neutralisation of every single unit of affinity.

Unsaturated compounds with an even number of unconnected units of affinity offer no objection to such an hypothesis; they may be charged with equal equivalents of opposite electricity. Unsaturated compounds with one unconnected unit, existing only at high temperatures, may be explained as dissociated by intense molecular motion of heat in spite of their electric attractions. But there remains one single instance of a compound which, according to the law of Avogadro, must be considered as unsaturated even at the lowest temperature, namely, nitric oxide (NO), a substance offering several very uncommon peculiarities, the behaviour of which will be perhaps explained by future researches.

But I abstain from entering into further specialities; perhaps I have already gone too far. I would not have dared to do it, had I not felt myself sheltered by the authority of that great man who was guided by a never-erring instinct of truth. I thought that the best I could do for his memory was to recall to the minds of the men by whose energy and intelligence chemistry has undergone its modern astonishing development, what important treasures of knowledge lie still hidden in the works of that wonderful genius. I am not sufficiently acquainted with chemistry to be confident that I have given the right interpretation, the interpretation which Faraday himself would have given, if he had been acquainted with the law of chemical quantivalence. Without the knowledge of this law I do not see how a consistent and comprehensive electrochemical theory could be established. Faraday did not try to develope a complete theory of this kind. It is as characteristic of a man of high intellect to see where to avoid

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going further in his theoretical speculations for want of facts, as to see how to proceed when he finds the way open. We ought therefore to admire Faraday also in his cautious reticence, although now, standing on his shoulders, and assisted by the wonderful development of organic chemistry, we are able, perhaps, to see farther than he did. I shall consider my work of to-day well rewarded if I have succeeded in kindling anew the interest of chemists in the electrochemical part of their science.

XLIII.—*On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride.*

By Frederick D. Brown, B.Sc., Demonstrator of Chemistry in the University Museum, Oxford.

Some eighteen months ago I communicated to the Society the results of some experiments upon the distillation of mixtures of carbon disulphide and benzene (this Journal, 1879, 547). The following paper contains a record of similar but improved experiments made with carbon disulphide and carbon tetrachloride.

In the former experiments the liquid was distilled from a retort or flask with short neck, the upper portion of which was unprotected. The vapour as it rose from the surface of the liquid and passed into the condenser was therefore subjected to a certain amount of cooling, which must have caused the condensation and return into the boiling mixture of a quantity of liquid richer in benzene than the vapour itself; hence the vapour which actually passed over was slightly poorer in benzene than that which was evolved by the liquid in ebullition. This source of error was avoided in the experiments now to be recorded, by the use of a copper still of the form and dimensions shown in the drawing on p. 311. It consists of a copper vessel, S, shaped like an ordinary tin can, but provided with a long neck, *ab*. This neck and the upper portion of the vessel are covered with a copper jacket, *ccc*, which communicates with the inner vessel by means of some small holes round the upper part of *ab*. This outer jacket is terminated below by a strip of copper placed obliquely to the axis of the vessel, and at its lowest portion is fitted a narrow tube, *dd*, which serves to connect the still with the condenser. The vapour rising from the liquid in the vessel S, passes through the holes at *a*, and then descending, passes out at *d*. The vapour as it rises is thus kept warm, and none of it is condensed until it has entered the outer jacket. Here a slight condensation is of no influence, as both vapour and liquid pass together into the receiver. The inclination of the

bottom of the jacket serves to prevent the accumulation of any liquid at that part. This form of still answered admirably for the purposes required, its only defect being that a kind of rapid evaporation took place in the interior vessel before the liquid began to boil. All the vapour thus formed passed into the outer jacket, so that a considerable quantity of liquid passed into the receiver before ebullition commenced. By rejecting the data obtained from the first fraction of the distillate, this defect, if such it can be called, was rendered entirely harmless.

The vapour was condensed in the ordinary apparatus which we owe to Liebig, and collected in the receiver which I described in the paper before referred to (p. 554).

The composition of the various fractions and other mixtures was, as before, determined by observing their densities, the temperature of 20° being employed instead of 19·80°. I have shown (this Journal, 1881, 202) that when carbon disulphide and carbon tetrachloride are mixed together, a certain expansion takes place, which is represented by a curve in the diagram accompanying that paper. From that curve, or rather from the original curve, which was drawn on a much larger scale, the values of the expansion were measured for every 5 per cent. of CCl_4 (reckoned in molecules). These values are contained in the following table (XIX). The third column of this table contains

TABLE XIX.

Percentage in mols. of CCl_4.	Vol. of mixture when sum of vols. = 1.	Calculated density.	True density.
0	1·00000	1·26575	1·26575
5	1·00109	1·29159	1·29019
10	1·00197	1·31593	1·31334
15	1·00268	1·33892	1·33534
20	1·00320	1·36068	1·35634
25	1·00362	1·38129	1·37630
30	1·00395	1·40084	1·39533
35	1·00416	1·41941	1·41353
40	1·00429	1·43708	1·43094
45	1·00423	1·45391	1·44779
50	1·00410	1·46996	1·46396
55	1·00391	1·48527	1·47949
60	1·00367	1·49991	1·49443
65	1·00338	1·51391	1·50881
70	1·00302	1·52732	1·52272
75	1·00260	1·54016	1·53617
80	1·00212	1·55248	1·54920
85	1·00164	1·56431	1·56175
90	1·00111	1·57568	1·57393
95	1·00056	1·58661	1·58572
100	1·00000	1·59712	1·59712

the density of the mixture, calculated on the supposition that no change of volume takes place, the fourth column, the true density, being the quotient of the numbers in the third column by those in the second. When it was desired to ascertain the percentage composition of any mixture, its density was observed and corrected to 20°, exactly as described in the papers above referred to; the corresponding percentage was then obtained from the table, on the assumption that between every 5 per cent. the density varied proportionally to the percentage.

The carbon disulphide employed was purified by agitation with mercury and with sulphuric acid and by distillation from the latter substance; it was then distilled several times, the first and last portions of the distillate being each time rejected. About 2 litres of the pure substance was thus obtained, of which the density at 20° (referred to water at 20°) was found to be 1·26575. The carbon tetrachloride used was obtained by carefully fractioning a large quantity of the best that could be purchased; finally two central fractions of about a litre each were taken for the experiments. The first boiled at 76·45—76·50°, the second at 76·50—76·60 (uncorr). The densities corrected to 20° of these fractions were 1·59703 and 1·59719 respectively. This close approximation shows that on distilling the whole quantity no great difference of density would be observed in the different portions. These two fractions were mixed together, and the density of the mixture found to be 1·59712 at 20°. This number, together with the corresponding one for the disulphide, forms the basis of the above table.

Before describing the various experiments made, it will be well for me to recall the object in view, namely, to find (1) the boiling point of every possible mixture of the two liquids; (2) the composition of the vapour evolved by any mixture when boiling. As was previously shown, these two series of data necessarily form a complete account of the distillation. In the former experiments some eight or ten fractions were collected at each distillation, and the composition of the liquid in the still at the moment of each removal calculated by successively subtracting each fraction from the original mixture. It is evident that as the distillation proceeds, the composition of the mixture in the still becomes more and more uncertain, owing to the accumulation of unavoidable errors. Further, the points on the final curve given by one distillation are so near together that three or four are nearly as good as eight or nine when the increasing inaccuracy is taken into account. In the following distillations, therefore, only four fractions were in each case collected.

The temperature of the vapour was measured by special thermometers, previously compared with the standards and corrected for index error; the thermometer was always so placed that only a small

portion of the mercurial column protruded above the cork; a correction on the score of unequal heating of the stem was therefore unnecessary.

First Distillation.—A mixture of carbon disulphide and carbon tetrachloride, having a density at 20° of 1·31149, and containing therefore 9·02 per cent. of CCl_4 (in molecules), was employed; 920·4 grams of this mixture were put in the still, and four fractions collected. The barometric pressure during the distillation was 745·6 (corr. and reduced to 0°).

The following table gives the details of the distillation, arranged as in the paper previously referred to:—

TABLE XX.

No of fraction.	Temperatures of distillation.	Weight of fraction.	Density corrected to 20°.	Percentage of CCl_4.
I.....	47·00—47·40	64·17	1·28783	4·21
II.....	47·40—47·48	69·14	1·29037	4·74
III.....	47·48—47·58	57·58	1·29150	4·98
IV.....	47·58—47·63	64·77	1·29263	5·22

Table XXI gives in the first column the percentage of CCl_4 in the still at the beginning, and at the moment of removal of each fraction. The numbers in this and the following similar tables were calculated by means of the formula—

$$M_1 = \frac{MW - mw\,\dfrac{7600 + 78\,M}{7600 + 78\,m}}{W - w\,\dfrac{7600 + 78\,M}{7600 + 78\,m}}$$

(see *loc. cit.*, p. 553). The second column contains the boiling point at the same moment; the third column gives the mean composition of the liquid in the still during the distillation of each fraction; and the fourth the composition of the fraction itself. The first two columns, therefore, give the first of the two relations sought for, and the last two the other.

TABLE XXI.

Percentage of CCl_4 in still.	Boiling point.	Composition of boiling liquid.	Composition of vapour given off.
9·0	47·00	9·2	4·2
9·4	47·40	9·6	4·7
9·8	47·48	10·0	5·0
10·2	47·58	10·5	5·2
10·8	47·63	—	—

The density of the liquid remaining in the still was found to be 1·32025, corresponding to 10·9 per cent. of CCl_4, a number which differs little from that found by the calculation, viz., 10·8.

Second Distillation.—1002·8 grams of a mixture having a density of 1·36242, and containing, therefore, 21·48 per cent. of CCl_4, were employed; the barometric pressure was 747·1 (corr. and red.). Tables XXII and XXIII give the results.

TABLE XXII.

No. of fractions.	Temperature of distillation.	Weight of fraction.	Density corrected to 20°.	Percentage of CCl_4 in fraction.
I	49·00—49·41	63·76	1·31292	9·91
II	49·41—49·58	59·74	1·31767	10·96
III	49·58—49·68	60·32	1·31888	11·23
IV	49·68—49·95	51·82	1·32003	11·48

TABLE XXIII.

Percentage of CCl_4 in still.	Boiling point.	Composition of boiling liquid.	Composition of vapour given off.
21·5	49·00	21·9	9·9
22·4	49·41	22·8	11·0
23·2	49·58	23·7	11 2
24·2	49·68	24·7	11·5
25·2	49·95	—	—

The density of the liquid remaining in the still was 1·37765, corresponding to 25·3 per cent. of CCl_4, which agrees well with 25·2 found by calculation.

Third Distillation.—871·5 grams of a mixture having a density of 1·42589 at 20°, corresponding to 38·55 per cent. of CCl_4, were now distilled, the reading of the barometer being omitted. Tables XXIV and XXV give the numbers obtained.

TABLE XXIV.

No. of fraction.	Temperature of distillation.	Weight of fraction.	Density corrected to 20°.	Percentage of CCl_4 in fraction.
I	52·00—53·40	66·5	1·34684	17·74
II	53·40—53·82	64·1	1·35930	20·72
III	53·82—54·58	74·9	1·36485	22·13
IV	54·58—55·26	75·2	1·37166	23·83

TABLE XXV.

Percentage of CCl_4 in still.	Boiling point.	Composition of boiling liquid.	Composition of vapour given off.
38·6	52·00	39·6	17·7
40·6	53·40	41·6	20·7
42·6	53·82	44·0	22·1
45·4	54·58	47·0	23·8
48·7	55·26	—	—

The liquid remaining in the still was found to contain 48·2 per cent. of CCl_4.

Fourth Distillation.—1020·0 grams of a mixture having a density of 1·51874, and containing 68·57 per cent. of CCl_4 were now distilled, the reading of the barometer being again omitted. Tables XXVI and XXVII give the numbers obtained.

TABLE XXVI.

No. of fraction.	Temperature of distillation.	Weight of fraction.	Densities corrected to 20°.	Percentage of CCl_4 in fraction.
I	61·00—62·90	68·1	1·43527	41·29
II	62·90—63·80	70·3	1·45462	47·11
III	63·80—64·80	76·6	1·46443	50·15
IV	64·80—65·80	71·4	1·47484	53·50

TABLE XXVII.

Percentage of CCl_4 in still.	Temperature of distillation.	Composition of boiling liquid.	Composition of vapour evolved.
68·6	61·0	69·8	41·3
70·9	62·90	72·1	47·1
73·2	63·80	74·5	50·2
75·8	64·80	77·0	53·5
78·3	65·80	—	—

The liquid remaining in the still contained 78·4 per cent. of CCl_4 compared with 78·3 found by calculation.

The four distillations described above suffice to determine the curve which gives the relation between the composition of the liquid in ebullition and its boiling point, as also the curve which represents the relation between the composition of the boiling liquid and that of the vapour given off. The first curve is furnished by the numbers in the first and second columns of Tables XXI, XXIII, XXV, and XXVII, those in the first columns being measured horizontally, those in the second vertically. The points thus obtained are marked (t) in the diagram; they admit of a curve being drawn through them very satisfactorily, as will be seen on reference to the diagram.

Table XXVIII contains the boiling points of the mixtures for every 5 per cent. of CCl_4 as measured from this curve. As no correction was made for the pressure, these numbers are not absolutely exact, but they will serve our purpose very materially in the sequel.

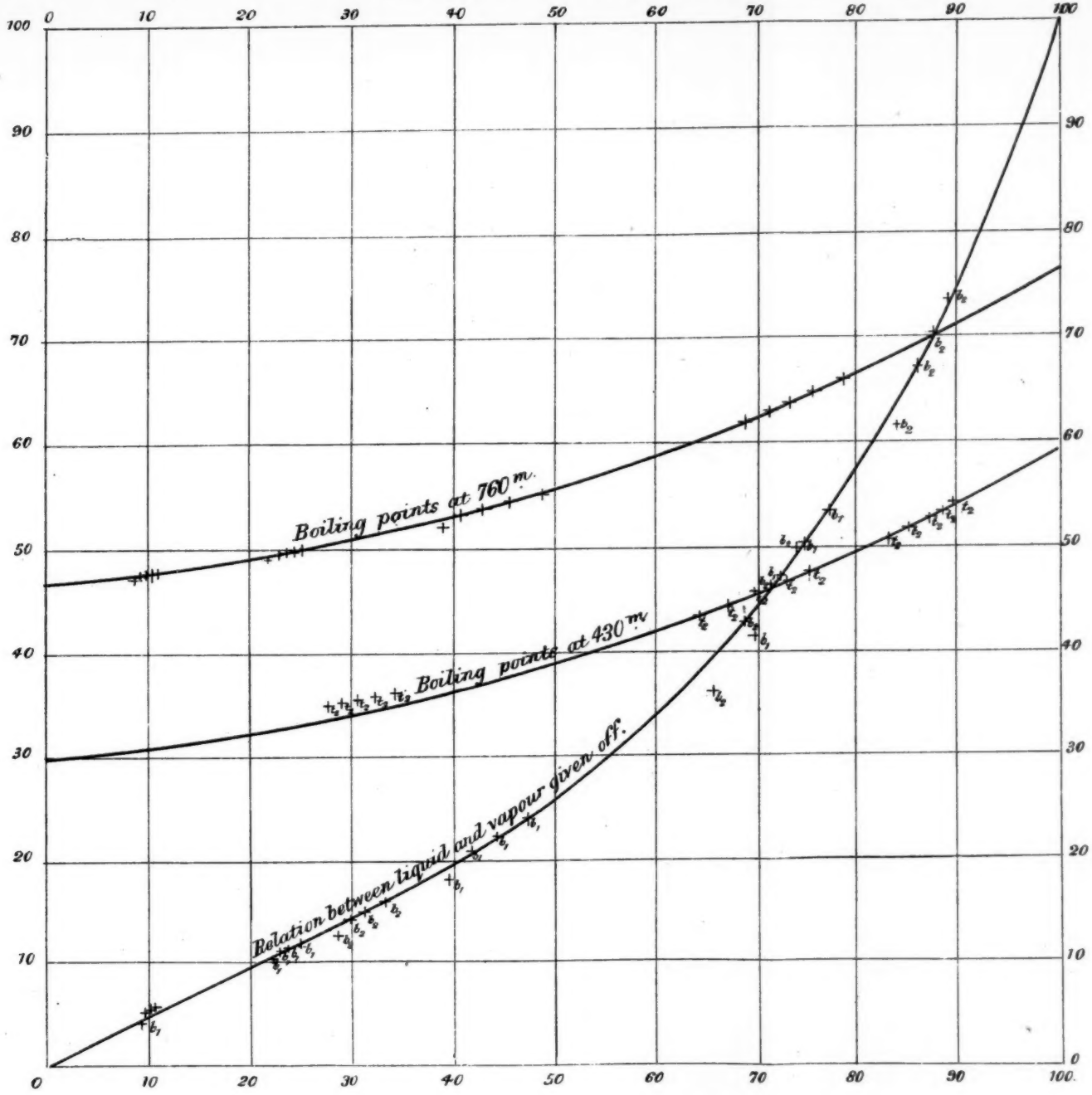
TABLE XXVIII.

Percentage of CCl_4.	Boiling point.	Percentage of CCl_4.	Boiling point.
0	46·6	55	57·3
5	47·0	60	59·0
10	47·6	65	60·7
15	48·2	70	62·5
20	49·0	75	64·4
25	49·9	80	66·5
30	50·9	85	68·8
35	52·0	90	71·3
40	53·2	95	73·8
45	54·4	100	76·5
50	55·8	—	—

The second curve is furnished by the numbers in the third and fourth columns of Tables XXI, XXIII, XXV, and XXVIII, those in the third column being measured horizontally, and those in the fourth vertically. The points thus obtained are marked (b_2). A continuous curve can be drawn through most of these points; those of the first distillation are, however, a little higher than the curve. It should be noticed that in each case the numbers derived from the first fraction of every distillation give points which do not conform to the line marked out by the others. This is evidently due to the fact that at first the distillation is irregular, the still not having yet assumed the proper temperature.

Table XXIX contains the composition of the vapour evolved by

FRACTIONAL DISTILLATION.



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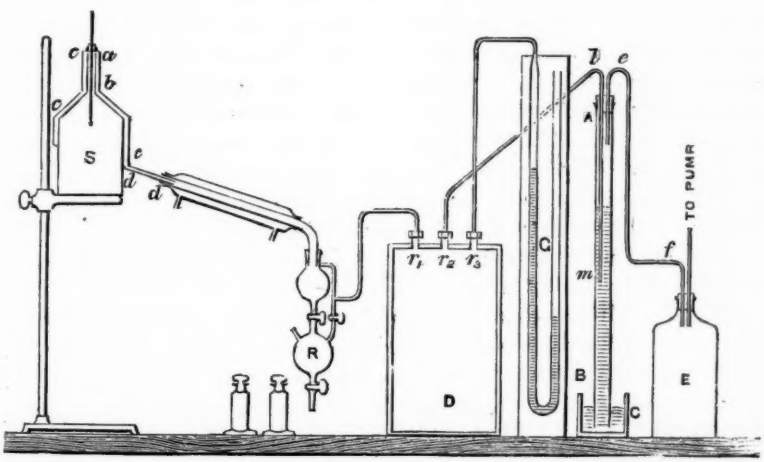
boiling mixtures from 5 to 5 per cent. of CCl_4 as measured from this curve.

TABLE XXIX.

Composition of boiling liquid.	Composition of vapour evolved.	Composition of boiling liquid.	Composition of vapour evolved.
5	2·4	55	29·6
10	4·8	60	33·8
15	7·1	65	38·7
20	9·4	70	44·5
25	11·8	75	50·8
30	14·2	80	57·6
35	16·8	85	65·1
40	19·6	90	74·6
45	22·6	95	86·8
50	25·8	100	100·0

The distillations described above were all carried out at the ordinary atmospheric pressure, but I thought it desirable to make another series at a considerably lower pressure. In order to effect this, the apparatus figured in the accompanying sketch was fitted up. S is the still, and R the receiver, the condenser being represented very short, with the view of economizing space. The receiver R is connected by means of small lead pipe and the union, r_1, with the iron cylinder, D; this cylinder is provided with two other unions, r_2 and r_3, one of which communicates with the gauge, G, the other with the tube AB. The upper end of this tube is closed with an india-rubber stopper, through which passes a second tube, *ef*, the other end of which enters the



bottle, E, which in its turn is connected with a water-jet pump, such as that described by Arzberger and Zulkowsky (*Annalen*, **176**, 327), and Fischer (*Ber.*, 1876, 747).

In using these pumps, care must be taken to prevent the water flowing into the apparatus, both when the greatest possible vacuum has been obtained and when the water is turned off. To avoid this difficulty the pump was furnished with a silk valve, such as is ordinarily used for air-pumps, but a metal valve would be better. The bottle, E, was introduced in order to catch any water which might pass this valve. The tube, AB, is a simple form of the apparatus devised by Victor Meyer for maintaining a constant pressure, with regard to which I may mention that an improved form has recently been described by O. Schumann (*Wied. Ann.*, **12**, 44). It will be seen from the drawing that when the pump has been working for some time, and the quicksilver in AB has risen above the extremity, m, of the tube, r_2lm, the pressure at m will always be measured by the height of the barometer, H, less the height, h, of m above the level of the mercury in the cistern, C; if, therefore, a greater pressure than this exists in the cylinder, D, air will bubble out at m, but as soon as the pressure has been reduced to $H - h$, the exit of the air at m will be stopped. The tube lm is of glass, and is sufficiently long to allow of the extremity m being placed at any point of AB, which tube must be more than 800 mm. in length. The tube r_2l is long and flexible (these details are not represented in the sketch). The gauge, G, is fixed on a firm support, opposite a cathetometer, by means of which the pressure can be read at any moment. This apparatus amply sufficed for the object in view, the mercury in the gauge never varying more than two or three millimeters when everything was in proper order. In employing it, the following are the main points to notice:—(1) the tube AB should be at least 3 centimeters in diameter; (2) the cylinder D should have a capacity of at least 50 or 60 litres; (3) a considerable leak should be established in the apparatus; this may be conveniently done by providing D with a screw plug, which can be loosened at will. The air then bubbles out at m in a continuous stream, whereas if the whole apparatus is nearly air-tight the bubbling at m is intermittent, and large oscillations take place in the gauge. The use of the receiver, R, was described in a former paper.

The following distillations of CS_2 and CCl_4 were now made at a pressure of about 430 mm.

Fifth Distillation.—The gauge was read at intervals during the distillation, and the mean pressure in the apparatus found to be 434·8 mm. (corr. and red.). 1006·0 grams of a mixture containing 27·81 per cent. of CCl_4 were placed in S, and four fractions collected as usual. Tables XXX and XXXI give the numbers obtained:—

TABLE XXX.

No. of fraction.	Temperature of distillation.	Weights of fractions.	Density corrected to 20°.	Corresponding percentage of CCl_4.
I.....	34·60—35·00	71·8	1·32400	12·42
II.....	35·00—35·40	76·2	1·33168	14·17
III.....	35·40—35·70	74·7	1·33541	15·02
IV.....	35·70—36·00	65·3	1·33953	16·00

TABLE XXXI.

Percentage of CCl_4 in still.	Temperature of distillation.	Percentage of CCl_4 in still.	Composition of vapour given off.
27·8	34·60	28·5	12·4
29·2	35·00	29·9	14·2
30·7	35·40	31·6	15·0
32·4	35·70	33·3	16·0
34·2	36·10		

The liquid remaining in the still was found to contain 34·5 per cent. of CCl_4, which is rather more than 34·2 per cent. found by calculation. This is probably owing to the leakage of the apparatus carrying off a certain amount of the more volatile carbon disulphide.

Sixth Distillation.—1033·0 grams of a mixture containing 64·14 per cent. of CCl_4 were heated in the still; the mean pressure in the apparatus being 430·3 mm. (corr. and red.). Tables XXXII and XXXIII contain the results:—

TABLE XXXII.

No. of fraction.	Temperature of distillation.	Weights of fractions.	Density corrected to 20°.	Corresponding percentage of CCl_4.
I.....	43·0—43·8	71·5	1·41725	36·07
II.....	43·8—45·4	89·5	1·43899	42·39
III.....	45·4—46·3	73·8	1·45100	46·00
IV.....	46·3—47·6	81·2	1·46351	49·86

TABLE XXXIII.

Percentage of CCl_4 in still.	Temperature of distillation.	Percentage of CCl_4 in still.	Composition of vapour given off.
64·1	43·0	65·4	36·1
66·7	43·8	68·2	42·4
69·7	45·4	71·0	46·0
72·3	46·3	73·8	49·9
75·3	47·6	—	—

The liquid remaining in the still was found to contain 75·7 per cent. of CCl_4, showing again a slight error from removal of CS_2.

Seventh Distillation.—The mean pressure during this experiment was 431·2 mm. (corr. and red.). 1213·1 grams of a mixture containing 82·94 per cent. of CCl_4 were put in the still. Tables XXXIV and XXXV contain the resulting numbers:—

TABLE XXXIV.

No. of fraction.	Temperature of distillation.	Weights of fractions.	Density corrected to 20°.	Corresponding percentage of CCl_4.
I.....	50·4—51·7	92·4	1·49882	61·53
II.....	51·7—52·5	95·3	1·51436	67·00
III.....	52·5—53·2	73·7	1·52372	70·37
IV.....	53·2—54·1	83·8	1·53252	73·64

TABLE XXXV.

Percentage of CCl_4 in still.	Temperature of distillation.	Percentage of CCl_4 in still.	Composition of vapour evolved.
82·9	50·4	84·0	61·5
85·0	51·7	86·0	67·0
86·9	52·5	87·7	70·4
88·4	53·2	89·1	73·6
89·9	54·1	—	—

The liquid remaining in the still contained 90·4 per cent. of CCl_4, again showing a loss of CS_2 during the distillation.

The first two columns of Tables XXXI, XXXIII, and XXXV serve to determine the curve representing the boiling points at the average pressure of 432 mm.; the points thus obtained are marked (t_2) on the diagram. They are at present insufficient in number; the curve drawn is therefore only approximate.

When I began to plot out the numbers in the third and fourth columns of the same tables, with a view to obtaining the curve representing the relation between the amounts of CCl_4 in the liquid and in the vapour, I was astonished to find that all the points lay nearly on the curve representing the same relation at the ordinary pressure, indeed when the slight error due to the gradual loss of CS_2 is allowed for, the coincidence of the two curves must be pronounced perfect; this will be seen on examining the diagram in which the points derived from the distillations at low pressure are marked (b_2). The process of fractional distillation seems therefore to be independent of the pressure under which it is effected; or to put the statement in a more general form, *when a mixture of two liquids is boiled, the composition of the vapour evolved is independent of the pressure under which ebullition takes place.* Since the two liquids were selected, as it were, by chance, it is highly improbable that this is an isolated case; but before asserting it to be a general law, it should of course be verified with many different liquids; to this verification I hope to contribute a few experiments as soon as an opportunity offers.

The curve which forms the locus of the points b_1 and b_2 is probably as accurate a representation of the relation between the liquid and its vapour as can be obtained by means of experiments of the nature of those described above. We are therefore in a position to test the value of the various theories of fractional distillation which have from time to time been put forward. I do not now propose to go into this question exhaustively, but merely to show that the explanation most generally accepted cannot be correct.

In 1863 Mr. J. A. Wanklyn (*Proc. Roy. Soc.*, **12**, 534; *Jahresb.*, 1863, 59) advanced the opinion that the proportion in which two liquids pass over when a mixture of them is distilled is dependent, firstly, as had previously been supposed, on their vapour-tensions at the boiling point of the mixture; secondly, on their relative weights in the mixture; and thirdly, on the vapour-densities of the substances in question. M. Berthelot (*Compt. rend.*, **57**, 430; *Jahresb.*, 1863, 60) in the same year made a few observations, which led him to the same conclusion; while Prof. T. E. Thorpe (this Journal, 1869, 544) seems to favour the same explanation. If T_1 and T_2 be the vapour-tensions of the two liquids at the boiling point of the mixture, M_1 and M_2 their molecular weights, W_1 and W_2 their relative weights contained in the mixture, while x_1 and x_2 are the relative weights of the vapours given off, the above law is expressed by the equation—

$$\frac{x_1}{x_2} = \frac{W_1 M_1 T_1}{W_2 M_2 T_2}. \qquad (1.)$$

If the vapour-tensions and vapour-densities of the two liquids are

inversely proportional, wrote Mr. Wanklyn, the mixture will distil unchanged; that is to say, when $M_1T_1 = M_2T_2$—

$$\frac{x_1}{x_2} = \frac{W_1}{W_2}.$$

The above equation is therefore an accurate representation of his views, and is, I think, that generally supposed to express the law which governs fractional distillation. It is easy to verify this law in the case of CS_2 and CCl_4.

Table XXXVI contains the vapour-tensions of the two substances as given by Regnault for temperatures between 25° and 80°; the fourth column gives the ratios $\frac{T_1}{T_2}$, and the fifth the differences between these ratios.

TABLE XXXVI.

Temperatures.	Tension of CCl_4.	Tension of CS_2.	Ratio of tensions.	Difference.
25	114·30	361·13	0·3165	—
30	142·27	434·62	0·3273	0·0108
35	175·55	519·66	0·3378	0·0105
40	214·81	617·53	0·3479	0·0101
45	260·82	729·53	0·3575	0·0096
50	314·38	857·07	0·3668	0·0093
55	376·29	1001·57	0·3757	0·0089
60	447·43	1164·51	0·3842	0·0085
65	528·74	1347·52	0·3924	0·0082
70	621·15	1552·09	0·4002	0·0078
75	725·66	1779·88	0·4077	0·0075
80	843·29	2032·53	0·4149	0·0072

An inspection of the numbers in the fifth column shows that we may consider the ratios to vary proportionally to the temperatures for intervals of 5°, and thus obtain readily the ratio for any temperature.

Dividing each side of (1) by $\frac{M_1}{M_2}$, we have—

$$\frac{\frac{x_1}{M_1}}{\frac{x_2}{M_2}} = \frac{W_1}{W_2} \times \frac{T_1}{T_2} \qquad (2),$$

that is, the ratio of the volumes of the vapours evolved equals the product of the ratio of the weights in the boiling liquid, by the ratio of the tensions at the boiling point.

Table XXXVII gives in Column I the percentage of CCl_4 in molecules for a few mixtures; in Column II the corresponding ratio of the

weights; in III the boiling points at 750 mm., as derived from the above experiments; in IV the ratio of the tensions; in V, the product of II and IV; in VI, the corresponding percentage composition which the vapour should have if equation (2) were true, and in VII the composition which it really has.

TABLE XXXVII.

I.	II.	III.	IV.	V.	VI.	VII.
20	0·5066	49·0	0·3649	0·1849	15·60	9·4
40	1·3509	53·2	0·3726	0·5033	33·48	19·6
50	2·0263	55·8	0·3771	0·7641	43·32	25·8
60	3·0394	59·0	0·3825	1·1626	53·76	33·8
80	8·1053	66·5	0·3947	3·1991	76·19	57·6

The numbers in the two last columns are widely different, showing that equation (2) does not express the law of the distillation.

Another possible law is that which I suggested in a former paper, viz., that the ratio of the volume of CCl_4 to the volume of CS_2 in the vapour evolved *by equal numbers of molecules* is equal to the ratio of their vapour-tensions at the boiling points of the mixture. The equation in this case would be—

$$\frac{\frac{x_1}{M_1}}{\frac{x_2}{M_2}} = \frac{\frac{W_1}{M_1}}{\frac{W_2}{M_2}} \times \frac{T_1}{T_2} \qquad (3),$$

$$\text{or } \frac{x_1}{x_2} = \frac{W_1}{W_2} \times \frac{T_1}{T_2}.$$

In Table XXXVIII the percentages of CCl_4 in the vapour, as calculated upon this hypothesis, are given in the second column, the observed values being again exhibited in the third :—

TABLE XXXVIII.

Percentage of CCl_2 in liquid.	Calculated percentage in vapour.	Observed percentage in vapour.	Calculated percentage with constant ratio.
20	8·36	9·4	8·05
40	19·90	19·6	18·92
50	27·38	25·8	25·93
60	36·46	33·8	34·43
80	61·22	57·6	58·33

As in the case of carbon disulphide and benzene the calculated numbers are not far removed from those obtained by experiment; the ratio of the vapour-tensions, however, increases so rapidly that the calculated numbers soon become too high. In the fourth column of the above table the calculated numbers are given when the varying ratios of the vapour-tensions are replaced by the constant ratio 3·5. These numbers agree much more exactly with those in the third column. Precisely the same result was set forth in the former paper on the distillation of CS_2 and C_6H_6. It would appear, therefore, that the general expression for the ratio of the weights of the two vapours given off is not—

$$\frac{x_1}{x_2} = \frac{W_1}{W_2} \times \frac{T_1}{T_2},$$

but

$$\frac{x_1}{x_2} = \frac{W_1}{W_2} C. \qquad (4.)$$

This form of the equation receives great additional support from the fact that the course of the distillation is the same at different pressures; take, for instance, the case of the mixture containing equal numbers of molecules of CS_2 and CCl_4. This mixture boils at 55·8° at the ordinary pressure; at a pressure of 432 mm. it boils at about 39°. Now the ratio of the tensions at 55·8° is 0·3771, while at 39° it is only 0·3459, yet the ratio of the volumes of each of the vapours evolved remains, as far as can be judged, absolutely unaltered. The ratio of the tensions, *as derived from Regnault's experiments*, cannot therefore enter into the expression sought for.

The constant number 3·5 is so near the mean ratio of the tensions that the question suggests itself whether the numbers obtained from Regnault's tables are not susceptible of correction or modification of some sort. These numbers express the maximum tension when the unmixed vapour occupies the entire space above the liquid, but in the case before us the vapour of one liquid is diffused through that of the other, and is diluted by it. Now Regnault himself showed, and his experiments are entirely in accord with theory, that the maximum tension of a vapour when diffused in a space containing a gas, differed considerably from that which ruled when the vapour was the sole occupant of that space. We ought therefore to substitute for the ordinary vapour-tensions those which hold good under the very different conditions of fractional distillation; these latter are at present unknown, but I hope shortly to have completed the necessary measurements, and we shall then be able to introduce the new ratios, and learn at the same time whether they vary with the temperature.

I should like before closing this paper to make a few remarks on the

experiments which were made by Mr. Wanklyn, by M. Berthelot, and by Prof. Thorpe, and which do not at all agree with the equation—

$$\frac{x_1}{x_2} = \frac{W_1}{W_2} C.$$

These experiments relate to mixtures of ethyl iodide and methyl alcohol, of carbon disulphide and ethyl alcohol, and of carbon tetrachloride and methyl alcohol; in each case a substance which does not mix with water is joined with methyl or ethyl alcohol which does. A very small quantity of water suffices under these conditions to break up the equilibrium of the solution, which resolves itself into two layers. Hence the presence of traces of water might be expected to render the distillation similar to that of two substances which do not mix; in this case (see former paper) the ratio of the quantities which pass over is constant, and is equal to the product of the ratio of the tensions by the ratio of the vapour-densities; now this is precisely what M. Berthelot and Prof. Thorpe observed. This view of the question is supported by the fact that the boiling points of mixtures of carbon disulphide or carbon tetrachloride with alcohol (methyl or ethyl) are often below that of the most volatile constituent, just as a mixture of two substances which do not undergo mutual solution boils at a temperature considerably below that of either; laws derived from these mixtures cannot therefore be considered as generally applicable.

XLIV.—CONTRIBUTIONS FROM THE LABORATORY OF THE ROYAL COLLEGE OF CHEMISTRY, SOUTH KENSINGTON.

On the Reduction of Cinnylic Alcohol.

By Frank Hatton and W. R. Hodgkinson.

When cinnylic alcohol is acted upon by sodium-amalgam in the presence of a large quantity of water, almost the sole product is β-phenylpropylic alcohol. When, however, an amalgam containing about 15 per cent. of sodium is employed and only a small amount of water, so that a strong sodic hydrate solution results, the reaction proceeds much further.

For the experiment cinnylic alcohol from storax, boiling between 248° and 252°, was digested in a steam-bath with sodium-amalgam of above-mentioned strength for three or four days, at the end

of which time water was added, and the whole distilled in steam. A considerable amount of an oily body came over with the water, which, on evaporation and distillation, gave a fraction boiling between 140° and 147°, having a strong odour of cinnamene, and giving on analysis:—

From I. 0·1520	CO_2.	0·5180
	OH_2.	0·1030
„ II. 0·0615	CO_2.	0·3195
	OH_2.	0·0938

	I.	II.	Theory for C_8H_8.
C	92·89	92·85	92·30
H	7·50	7·27	7·69

The aqueous portion of the distillate separated from the cinnamene was neutral to test-papers, but rapidly decolorised a solution of potassic permanganate. It was therefore treated with a solution of this salt until a slight colour remained, when it was evaporated to dryness on a steam-bath. The resulting potassic salt gave all the reactions of formic acid. It was converted into a lead salt, and a lead determination made:—

I. 0·2800 substance gave 0·2120 PbO.
II. 0·5310 „ 0·5410 $PbSO_4$.

	I.	II.	Theory.
I	70·00	69·67	69·80

The ultimate reactions may therefore be represented thus:—

$$C_6H_5.CH:CH.CH_2.OH + H_2 = C_6H_5.CH:CH_2 + CH_3.OH.$$

Neither α- nor β-phenylpropylene appears to be formed when the cinnylic alcohol is nearly anhydrous, although the latter is formed when considerable quantities of solutions of cinnylic alcohol in warm dilute potassic hydrate are treated with zinc.

XLV.—*Organic Matter in Sea-Water.*

By William Jago.

On page 133 of the Sixth Report of the Rivers Commission, it is stated that the proportion of organic elements in sea-water varies between such wide limits in different samples as to strongly suggest that much of the organic matter consists of living organisms so

minute and gelatinous as to pass readily through the best filters. It was suggested to me by Dr. Frankland that further investigation of the quantity and properties of this organic matter would be of service; of which suggestion this paper is one of the results.

Through the kindness of Mr. J. P. Knight, manager of the London, Brighton, and South Coast Railway, I was enabled to make the following experiments on water collected in mid-channel between Newhaven and Dieppe by the engineers of the Company's boats. Written directions accompanied each of the stoppered glass carboys used, to the effect that the sea-cock in the engine-room was to be allowed to run for a minute; the carboy was then to be filled, emptied and refilled, and then immediately to be tied down with a piece of washleather and forwarded. I have to thank Captain Harvey, the Marine Superintendent at Newhaven, for personally seeing that these directions were attended to.

Microscopic examinations were made from time to time with the highest power at my command (an eighth), but I was unable to detect infusoria by means of it.

The water was examined by the combustion method, and also the nitrogen evolved as ammonia and as albuminoïd ammonia, was estimated. The following table (p. 322) gives the result of analyses extending over a period of about two months.

These samples collected in approximately the same place show a considerable amount of variation; but in no case does the amount of organic N exceed that of organic C, although the ratio varies between the limits of 5·3 and 1·29, the mean being 3·2.

The water being sometimes not perfectly clear, an experiment was made in order to determine whether the solid matter contained an important quantity of organic constituents. Two litres of the water of March 18th were filtered through a Casamajor's funnel with a disc of Swedish paper one inch in diameter, and the suspended matter dried at 100° C. and weighed. Its amount equalled 0·900 part per 100,000. A litre of the water was placed in a tall cylindrical jar, and allowed to subside; the clear water was syphoned off and examined. The sediment with 60 c.c. of clear water was also tested, allowance being made for the organic matter in the water. The following are the results:—

	Organic			Nitrogen as	
	Carbon.	Nitrogen.	Ratio.	Ammonia.	Albuminoïd ammonia.
The clear water..	0·210	0·075	2·8	0·006	0·004
The sediment....	0·036	0·008	4·5	—	—

It should be mentioned that this experiment was commenced on the 2nd April, and the water allowed to stand for six days before syphoning

Results expressed in Parts per 100,000.

Date.	Organic carbon.	Organic nitrogen.	Ratio.	Nitrogen as ammonia.	Nitrogen as albuminoid ammonia.	Remarks.
March 1st	—	—	—	0·00025	0·003	
„ 4th	0·536	0·137	3·8	0·00015	0·004	
„ 6th	0·728	0·149	4·8	0·00	0·008	
„ 9th	0·373	0·102	3·6	0·0005	0·014	Water turbid.
„ 11th	0·309	0·104	2·9	0·0006	0·006	„ fairly clear
„ 13th	0·322	0·103	3·1	0·0002	0·015	„ „
„ 16th	0·290	0·073	3·9	0·0006	0·014	„ slightly turbid.
„ 18th	0·264	0·112	2·3	0·00025	0·010	„ fairly clear.
„ 20th	0·452	0·163	2·8	0·0002	0·004	„ clear.
„ 23rd	0·287	0·103	2·8	trace	0·009	„ „
„ 27th	1·188	0·222	5·3	0·005	0·038	„ very turbid.
„ 30th	0·216	0·075	2·9	0·0003	0·012	„ clear.
April 1st	0·494	0·094	5·2	trace	0·003	„ „
„ 3rd....	—	—	—	0·00	0·003	„ „
„ 6th....	0·228	0·128	1·78	0·00	0·010	Syphoned water used.
„ 10th	—	—	—	0·0013	0·0035	Water clear.
„ 13th	0·315	0·220	1·43	0·0001	0·003	Syphoned water used.
„ 16th	0·151	0·117	1·29	0·0002	0·002	„ „
„ 19th	—	—	—	trace	0·001	„ „
„ 22nd ...	—	—	—	trace	0·001	„ „
„ 24th	—	—	—	trace	0·002	„ „

off the supernatant liquid. The loss of organic N and of organic NH_3, together with the increase of free NH_3, suggests a breaking up of some of the organic constituents.

The sediment being practically inorganic, most of the succeeding analyses were made in the syphoned water. An examination of the tabulated results given above shows that the ratio of the organic nitrogen, to that evolved on distillation with alkaline permanganate, is very much higher than that in the case of fresh waters. This, indicating that the organic matter in sea-water is more stable than that in potable waters, led me to endeavour to ascertain by experiment how far a change in the condition of organic matter from organic compounds in solution to organisms in suspension in a water affected the results of the various methods of analysis in common use. Two series of experiments, besides some isolated ones, were made on hay solutions; but as the results in every case were similar, those of one series only are appended.

The solution was made by boiling hay in water for about half an hour, and then filtering.

This was placed in a glass flask and covered with a beaker. An estimation of organic matter was made in 50 c.c. by evaporation and combustion immediately the solution was made up on May 11th; it was then found to contain:—

Organic carbon....	28·426	per 100,000.
„ nitrogen..	2·420	

The following determinations represent the nitrogen evolved as free and also as albuminoïd ammonia, and the quantity of oxygen absorbed in accordance with the oxygen process of Dr. Tidy respectively during one and six hours. The nitrogen experiments were made by taking 10 c.c. of the hay infusion, and adding previous to distillation 500 c.c. of water from the Brighton Water Company's mains, which is practically of constant composition. A deduction was made for the amount of nitrogen in the Brighton water as albuminoïd ammonia, which amounts to ·001 part per 100,000.

For each determination by the oxygen process 5 c.c. were taken, and 20 c.c. of potassium permanganate solution, 1 c.c. of which = ·001 oxygen added, the one sample being titrated with hyposulphite at the end of one hour; the second at the expiration of six hours.

To the water of May 11th but 10 c.c. of permanganate were added for the first determination; but as at the end of the hour the solution was almost decolorised, 20 c.c. were used in all following experiments (p. 324). The sample in which the second estimation was made stood only five hours.

On May 31st a second combustion of 50 c.c. was made, which gave—

Organic carbon....	22·552	per 100,000.
„ nitrogen..	2·350	

I have since much regretted that intermediate combustions were not made, in order to observe the rate at which this decrease of carbon took place, a result probably of oxidation into carbon dioxide. It will be noticed that the experiments with permanganate are somewhat similar to those of Kingzett (*Chem. Soc. J.*, 1880, 15), but though the results closely agree with his, the experiments were made quite independently, and with a different object in view.

As surmised, the capacity of resistance of the organic matter to the action of agents of limited oxidation, as in the oxygen and albuminoïd processes respectively, diminishes rapidly with the development of organisms, and the changes which accompany their presence. The free ammonia entirely disappears, and the nitrogen as albuminoïd ammonia is steadily reduced from 0·912 to 0·257, the actual quantity of organic nitrogen present in the liquid remaining practically the same. The oxygen absorbed decreases from 34·09 on May 12th, to

Dates.	Nitrogen as		Oxygen required after		Remarks.
	Ammonia.	Albuminoïd ammonia.	One hour.	Six hours.	
May 11th...	0·1	0·912	17·640	33·74	Special quantities used for oxygen process.
„ 12th...	0·1	0·75	24·20	34·090	
„ 13th...	0·1	0·75	25·256	33·500	
„ 14th...	0·09	0·70	22·452	33·468	
„ 15th...	—	—	20·290	29·656	Bacteria in large quantity.
„ 16th...	—	—	19·122	28·456	
„ 17th...	—	—	18·304	27·046	
„ 18th...	0·012	0·4	16·600	24·950	
„ 19th...	—	—	16·634	24·400	
„ 20th...	trace	0·3	15·830	22·855	Solution began to have strong putrescent odour.
„ 21st...	„	0·275	15·736	23·244	
„ 22nd...	„	0·3	15·662	22·934	
„ 24th...	„	0·25	14·354	21·420	
„ 25th...	—	—	14·352	21·698	
„ 26th...	trace	0·3	—	—	
„ 27th...	„	0·26	13·810	—	Towards end of experiment became turbid and deposited sediment.
„ 28th...	absent	0·25	13·964	22·264	
„ 29th...	—	—	13·710	—	
„ 31st...	—	—	13·774	21·710	

21·71 on May 31st, the lesser quantity indicating a diminution of 36·4 per cent. of the higher. During the same time a diminution of 19·3 per cent. of organic carbon + nitrogen has taken place.

A number of experiments were made by the oxygen process on sea-water, but the presence of bromides in such large quantity rendered the results unsatisfactory. The estimations were made in accurately stoppered bottles, to avoid volatilisation of bromine. Instead of standardising the hyposulphite on pure water and permanganate, a solution was made of ignited sodium chloride and potassium bromide in the proportions in which they are present in sea-water. In order, however, to have excess of permanganate solution present, it was necessary to add much more of the solution than was used of sea-water: for instance, the following quantities were used in most of the experiments:—Sea-water, 10 c.c.; permanganate, 25 c.c. On the water of March 4th, after standing 19 hours, it was found that 26·15 c.c. of hyposulphite were required. A duplicate sample gave the result of 26·20 of hyposulphite, while the standard required 26·40 of hyposulphite, the results calculated from these are respectively 0·25 and 0·19 part of oxygen absorbed per 100,000, giving a mean of 0·22.

The experiments, so far as they have gone, show the organic matter of sea-water to be much more capable of resisting oxidising agents than that of common fresh waters. This fact, and also the behaviour of the hay infusion, are in my opinion evidence strongly in favour of the supposition that the matter in sea-water is not only organic, but also organised and probably alive. They at least show the behaviour of such organic matter to be much more like that of a solution containing living organisms than the same solution when known to be devoid of them.

Subjoined is a table showing the ratio of organic nitrogen to organic nitrogen evolved as ammonia in several waters; and also the ratio of the organic carbon + nitrogen to the oxygen required in the permanganate process. The results, which are expressed in parts per 100,000, are calculated from those given in the Sixth Report of the Rivers Commission, p. 253 and in Dr. Tidy's paper in the Chemical Society's Journal of 1879, p. 101).

	Organic nitrogen.	Nitrogen as organic ammonia.	Ratio.	Organic nitrogen + Carbon.		Oxygen absorbed.	Time allowed to stand.	Ratio.
Chelsea	0·023	0·0058	3·9	0·153	—	0·087	3 hours	1·7
W. Middlesex ..	0·026	0·0046	5·6	0·146	—	0·025	„	5·9
Southwark	0·021	0·0093	2·2	0·157	—	0·075	„	2·0
Lambeth	0·038	0·0069	5·5	0·187	—	0·063	„	2·9
New River	0·015	0·0046	3 2	0·077	—	0·038	„	2·0
E. London	0·046	0·0069	6·6	0·185	—	0·057	„	3·2
Kent	0·017	0·0034	5·0	0·073	—	0·010	„	7·3
Hay, May 11th.	2·42	0·912	2·6	May 12th,	30·846	34·090	6 „	0·9
„ „ 31st.	2·35	0·257	9·1	„ 31st,	24·902	21·710	„	1·1
Lea, March 16th	0·073	0·014	5·2	Lea March 4th	0·673	0·22	19 „	3·0
„ April 16th.	0·117	0·002	58·5					
Mean of 14 analyses....	0·120	0·0081	14·8					

I have at present a series of experiments in progress, with the view of ascertaining the capability of the organic matter in sea-water to resist oxidation by atmospheric air, as compared with that of other waters. I also hope to be able to make some reliable estimations of the oxygen-absorbing power of this organic matter by a modification of Dr. Tidy's oxygen process, and at some future time to have the honour of laying the results of these experiments before the Chemical Society.

XLVI.—*On the Action of Compounds inimical to Bacterial Life.*

By William M. Hamlet.

The study of these minute forms of life shows us that their presence is much more common than is usually imagined, and if they are so intimately associated with the spread of infectious diseases as Pasteur's brilliant researches have lately shown them to be, it may not be altogether inappropriate to give an account—rather fragmentary, it is true—of the behaviour of certain species in the presence of different reagents under similar conditions.

The products arising from the life of various organisms in organic compounds have perhaps been more fully studied than the effect of various compounds upon the bacteria themselves, the effect, for example, we should expect to find on comparing the known behaviour of anæsthetics and poisons upon the higher animals.

Crace-Calvert's experiments upon this subject stand almost alone, and may be found in the *Chemical News*, **22**, 281, *et seq.* He there shows that by exposing solutions of disinfectants containing egg-albumen and flour-paste to the atmosphere, and allowing them to become invaded by living organisms, bacteria make their appearance after a number of days, the period varying in each case with the disinfectant tried.

These experiments were all made in open test-tubes and bottles free to the air, and liable to both oxidation and evaporation. His results show that where 2 per cent. of cresylic or carbolic acid was employed in the organic test-fluid, it was preserved from all offensive odour, and the bacteria died off and disappeared from view. But it will be observed that the exposure to the air allowed oxidation to go on along with the action of the disinfectant, so that it is not quite clear as to what share the disinfectant had in the matter; besides this, the paper referred to states that in some of the experiments the liquids employed "dried up and became quite hard."

Now bacteria require a moist medium for their regular development, notwithstanding the length of time they may be preserved in the zooglœa stages of their existence—conditions under which they resist the action of a large number and variety of compounds in solution, bodies that would for the most part seriously check, if not altogether destroy, many of the higher forms of life.

This power of resistance, coupled with the fact that bacteria may even be desiccated and reduced to an impalpable powder without being killed, shows pretty clearly, I think, that they may exist for an indefi-

nite length of time, and may easily be carried about in the air without losing their reproductive faculties. Consequently, when favourable conditions surround them, it is simply a question of time for their development and vitality to become manifest.

To eliminate this extraneous oxidation and to supply the lack of moisture in the experiments referred to, so essential to their growth, I prepared a large number of flasks, similar to those used by M. Pasteur himself, and which may be found figured and described in his *Études sur la Bière*, p. 81. These held about a quarter of a litre, and were in every way adapted for this research, as by the double tubulure the action of both gases and vapours, as well as liquids, can be observed with facility. The liquids employed were Pasteur's fluid with sugar, beef-tea, hay-infusion, urine, brewer's wort, and extract of meat. Each flask was about half filled, and boiled for ten minutes, whereby all previously-existing life was destroyed; while the steam was still escaping from the fine orifice of the drawn-out tube a plug—sometimes of glass-wool or of asbestos—was inserted, and the flask left to cool down to 15·5° C. By this method, which is, in effect, that of Appert and Pasteur, and equivalent to the glycerin chamber of Tyndall, we obtain a liquid which is entirely free from life, and may be kept indefinitely, without fear of any change taking place. At 15·5° each flask was impregnated by means of a fine glass tube with bacteria, which had been previously cultivated in hay-infusion or Pasteur's fluid. This was found to be the best method to employ where we want to inoculate a given liquid without the risk of introducing other kinds of life, and thus the errors arising from spontaneous oxidation and evaporation were entirely eliminated, so that the precise effect of any reagent or disinfectant could be studied.

To 150 c.c. of Pasteur's fluid 1 c.c. of meat solution containing bacteria was added, and a current of pure hydrogen was passed over the liquid contained in the flask. The tubes were now closed, and the flask placed in a warm chamber, kept at a constant temperature of 25° by a gas-regulator, for three days. On examination the solution contained bacteria in abundance.

The same volume of Pasteur's fluid was taken and oxygen passed over the liquid, the flask then closed and left for three days. A thick film was found on the surface, due to micrococci chiefly. The gas was then examined and found to be entirely absorbed by caustic potash-solution, and proved to be carbon dioxide. The oxygen had evidently been consumed by the action of the bacteria and displaced by the carbon dioxide. The life in the flask was very abundant. A flask was prepared in the same way as the last, and chlorine gas passed over the liquid containing bacteria. Both at the end of the operation and three days afterwards no life was visible.

15 c.c. of a 5-volume solution of hydric peroxide was added to a flask containing Pasteur's fluid, in which there were plenty of bacteria. In 24 hours the liquid was examined, and no bacteria were seen moving.

A flask containing 150 c.c. of hay-infusion was connected with a reservoir of carbonic oxide, and the gas passed into the flask for several minutes. After the lapse of three days no effect was observed upon the bacteria; they were as numerous and lively as before.

Marsh-gas, nitrogen, and sulphuretted hydrogen were each tried, and were found to have no effect upon the life of bacteria; while in flasks containing bacteria in solution, and into which nitric oxide and sulphur dioxide were respectively passed, the liquids remained free from moving bacteria.

The action of various salts and organic acids was next tried, and the following compounds in the form of a 5 per cent. solution in each case were found to have no decided effect either one way or the other, the bacteria developing readily in all of them.

Series A.—Potash, soda, ammonia, olive oil, castor oil, cod-liver oil, potassic bisulphite, ammonic succinate, ammonic sulphate, potassic tartrate, Rochelle salts, potassic bitartrate, tartaric acid, benzoic acid, citric acid, oxalic acid, potassic bromide, potassic iodide, potassic chlorate, potassic chloride, potassic permanganate, sodic hyposulphite, glycerin, succinic acid, laudanum, potassic formate, tannin, acetic acid, ethylic and methylic alcohols.

Those compounds which were found to have effect upon bacteria, hindering their growth, but not entirely preventing their development, are the following:—

Series B.—Potash and ammonia-alum, ferrous sulphate, ferric chloride, magnesic and aluminium chlorides, bleaching powder, camphor (as Spt. Camphoræ, B. P.), salicylic acid, chloroform, creosote, and carbolic acid.

In these cases 5 per cent. of the reagent had a decided effect in arresting the development of bacteria, and sometimes when only 2 per cent. was present. The bacteria were observed to become very sluggish, and to exhibit the Brownian movement only. The action of creosote had been previously recorded by Bechamp (*Compt. rend.*, **68**, 451) who shows that the life of bacteria is hindered but not extinguished by solutions containing creosote.

With regard to the action of chloroform as affecting the vitality of bacteria, it has been stated by Müntz (*Compt. rend.*, **80**, 1251) that they cannot exist in the presence of $2\frac{1}{2}$ per cent. of chloroform. He there states that 200 c.c. of milk were taken, and 5 c.c. of chloroform added, and that no organisms were visible after four months. From this and some similar experiments he infers that chloroform is a reagent

by which chemical and physiological ferments may be distinguished one from another, meaning thereby that the supposed fatal influence of chloroform enables us to draw the line between those ferments, such as diastase, the saliva, gastric juice, &c., on one hand, and those having an organised structure and means of reproduction, such for instance as the bacteria concerned in the phenomenon of nitrification. As I was then searching for a compound which should limit if not altogether suppress bacterial life, I repeated these experiments of Müntz, and obtained somewhat different results.

200 c.c. of milk and 5 c.c. of chloroform were placed in a flask, and 1 c.c. of a solution of extract of beef alive with bacteria added. The flask was kept at 25° and examined four days afterwards. The bacteria were abundant and lively.

The same result was obtained with the following solution:—

200 c.c. of fresh urine and 2 c.c. of chloroform, 10 grams of cane-sugar in 200 c.c. of water, with 1 gram of chalk and 1 gram of cheese 5 grams of gelatin and starch in 200 c.c. of water.

In the microscopic examination of these liquids at various times it was found that some species of bacteria were motionless, while some were possessed of more than a Brownian movement, and swam freely about in all directions.

To put the matter to the most rigorous test, I made up some easily-putrescible liquids, similar to those employed by Müntz, which I proceed to describe.

I. 200 c.c. of fresh milk at 15° was placed in a flask marked A, and 1 c.c. of a liquid known to contain *B. termo* and *M. crepusculum* was added. The flask was then closed, and kept at a temperature of 25° for 12 hours. To the milk, now containing numberless bacteria, was added 6 c.c. of Duncan and Flockhardt's chloroform, and the flask returned to the warm chamber. Five days afterwards the contents of the flask was examined, and the bulk of the bacteria were noticed huddled together in shoals, for the most part motionless, while others were moving about in different directions.

II. 200 c.c. of urine at 15° was impregnated with *B. termo*, *M. crepusculum*, and *B. punctum*. At the end of 12 hours 6 c.c. of chloroform, and the flask (B) was then closed and placed in the chamber, and kept at 25° for five days. On examination on the morning of the fifth day the bacteria were alive and rapid in their movements.

III. In this case 10 grams of cane-sugar were dissolved in 200 c.c. of distilled water, 1 gram of chalk, and 4 grams of old cheese added; the solution was impregnated with bacteria as in the previous experiment, and dosed with 6 c.c. of chloroform. On examination four days afterwards, with the exception of a few *B. termo*, the majority of the bacteria were swimming easily to and fro across the field.

IV. 200 c.c. of milk, 1 gram of egg-albumen, and 1 gram of cane-sugar was impregnated with the same species of bacteria as in the other experiments, chloroform then added, and examined four days afterwards. Large numbers of living bacteria were seen swimming all over the field.

V. 2 grams of pure carbolic acid in crystals were dissolved in 200 c.c. of Pasteur's fluid, which was known to contain *B. punctum*, *B. termo*, and *M. crepusculum*. The mixture was set aside for five days in the warm chamber at 25°. Upon examination there was a slight diminution in the number of moving bacteria, but still a considerable number were swimming to and fro.

VI. 10 grams of crystals of carbolic acid were dissolved and mixed with 200 c.c. of Pasteur's fluid, and sown with bacteria from the same stock as in the last experiment. At the end of five days very few showed signs of movement, and the majority were lying dormant in shoals.

VII. 5 c.c. of the solution from VI was placed in a flask containing 100 c.c. of recently boiled Pasteur's fluid. In two days the solution was full of life, bacteria swimming about freely.

VIII. 1 c.c. of each of the solutions in flasks I, II, III, IV, and V was placed into a flask along with 100 c.c. of Pasteur's fluid with sugar, and after having been kept in the warm chamber for 48 hours, each of the five solutions was found to be swarming with life.

These results show that amounts of chloroform, phenol, and creosote, varying from $\frac{1}{4}$ to 3 per cent., do not destroy bacteria, although their functional activity is decidedly arrested while in contact with these reagents. To use a homely illustration, bacteria may be pickled in creosote and carbolic acid, without being deprived of their vitality. Take them out of pickle, and surround them with suitable nourishment in the form of albuminous solutions, and their life proceeds uninterruptedly as before.

During his admirable researches, Pasteur recognised a distinction between those members of the bacteria family which are incapable of an existence without oxygen, and those on the other hand which go on living without air or oxygen. The former he terms aërobian; the latter anaërobian. Upon both classes of bacteria oxygen has a most important action. To the anaërobian oxidation is rapid and fatal as a poison to the higher animals, while the aërobian less easily oxidised are resolved by complete oxidation into nitrogen, carbon dioxide, and water.

We may conclude, therefore, that those bodies which destroy bacteria are those capable of exerting an immediate and powerfully oxidising action, and it seems, after all, but stating a truism to say that (extremes of temperature, of course, excepted) it is active oxygen

which must be regarded as the greatest known enemy to bacteria life, whether from the action of chlorine, nitric oxide, ozone, or peroxide of hydrogen. It also follows that these bodies are the best disinfectants.

XLVII.—*On the Amylamines Corresponding to the Active and Inactive Alcohols of Fermentation.*

By R. T. Plimpton, Ph.D.

Since Pasteur's discovery in 1855, that the amyl alcohol of fermentation is separable into two, differing in their action on polarised light, the subject has been investigated by many chemists, notably by Frankland and Duppa, Pedler, Chapman, Erlenmeyer and Hell, Pierre and Puchot, N. Ley, Balbiano, and Le Bel. Their researches have shown, in the first place, that the two alcohols and their corresponding derivatives differ slightly in their physical properties, and that the compounds obtained with the optically active alcohol are also optically active (Wurtz).

As to the question of constitution, Erlenmeyer (*Ann. Ch. Pharm.*, Supp. **5**, 337) proved, by a comparison of the valeric acid obtained from amyl alcohol with an acid obtained from isobutyl cyanide, that fermentation amyl alcohol contains isobutyl carbinol, and until quite recently the active and inactive alcohols were generally regarded as "physically" isomeric modifications of the same.

Indications of a difference in their chemical structure were, however, given by the experiments of Pedler (this Journal [2], **6**, 74), who found that the active alcohol when oxidised with chromic acid under certain conditions, gives carbonic and acetic acids, together with valeric acid, the sole product of the oxidation of the inactive alcohol; and Erlenmeyer was led by his researches on valeric acids from different sources, to regard the active alcohol as probably ethyl-methylic ethyl alcohol (pseudobutyl carbinol), $\begin{matrix}C_2H_5\\CH_3\end{matrix}\!>\!CH—CH_2OH$. Finally, his view has been confirmed and the question set at rest by the synthesis of ethyl-methyl-acetic acid, found by R. Saur (*Ber.*, **8**, 1037) to be identical with active valeric acid.

The active and inactive alcohols having been thus proved to be chemically different, it becomes more than ever desirable to follow out the isomerism of their corresponding derivatives. In this direction, a

comparison of the properties of the active and inactive amylamines appeared likely to prove of interest, particularly because it was to be expected that characteristic differences would be observed in the secondary and tertiary amines containing two and three active or inactive groups.

A study of the bodies in question has shown that the active amylamines, besides slightly differing from the inactive, in boiling point and specific gravity, form salts which crystallise only with great difficulty, whereas the inactive salts crystallise remarkably well. The active salts are the more soluble, and in some cases dissolve in liquids in which the corresponding inactive salts are quite insoluble.

The action of the active amines on polarised light is remarkable, mono-amylamine being levogyrate, but di- and tri-amylamine dextrogyrate. The triamylamine obtained was very active, and rotated 11 times as much as the alcohol from which it was derived.

Inactive Amylamines.

In order to obtain active amyl alcohol, I followed the process of M. Le Bel (*Compt. rend.*, **77**, 1021), and distilled the alcohols with gaseous hydrochloric acid, which first attacks the inactive alcohol. At the end of about six weeks, the greater part of the 3 kilos. of alcohol employed had been converted into chloride, but the residuary alcohol, which had originally rotated 1 degree for a length of 10 cm., showed only a rotation of 2—20° for the same length. The experiment was therefore a failure as far as the preparation of the active alcohol was concerned, but it furnished a quantity of inactive amyl chloride, which was employed for the preparation of the inactive amylamines. To this end the chloride which distilled principally at 100·5°, and did not rotate perceptibly in a tube 10 cm. long, was heated for some hours at 140—150° with its own volume of saturated alcoholic solution of ammonia in a digester. The resulting crystalline mass, consisting chiefly of the hydrochlorides of di- and tri-amylamine, was freed from ammonium chloride by treatment with alcohol. The dry hydrochlorides were then distilled with potash, and the portion coming over below 110°, after having been converted into hydrochloride and evaporated once or twice to drive off a small quantity of amyl alcohol, yielded, after repeated rectification over potash, the pure amylamine boiling at 96—97° (barometer 766 mm.). Its specific gravity at 0° is 0·7678, at 22·5° 0·7501. It had no action on polarised light.

The *hydrochloride* is soluble in alcohol, and very easily so in water. A chlorine estimation gave Cl = 28·85. Calculated 28·74.

The *platinochloride* separates from hot water in scales. At 14° 100 parts water dissolve 1·7 parts of the salt. It is nearly insoluble in alcohol. An estimation of platinum gave: Pt = 33·43 per cent. Calculated 33·66.

The *aurochloride* when precipitated by addition of a solution of gold chloride to the hydrochloride, forms scales soluble in alcohol and ether.

By spontaneous evaporation of a solution in dilute alcohol, small flat crystals are obtained, in the form of a rhomb with its acute angles truncated.

The inactive *diamylamine*, obtained by fractional distillation of the residue, after separation of monamylamine, or from the pure recrystallised hydrochloride, boiled at 185—186° (uncorr.). It is insoluble in water. At 0° its sp. gr. is 0·7878; at 14°, 0·7776.

The *hydrochloride* crystallises from hot water in beautiful laminæ, slightly soluble in cold water, soluble in alcohol, but quite insoluble in ether. This affords a means of separating inactive di- from tri-amylamine, as the hydrochloride of the latter is easily soluble in ether. An estimation of chlorine gave: Cl = 18·31 per cent. Calculated 18·34.

A crystal of the pure hydrochloride of diamylamine placed on the surface of distilled water moves about, spinning with great rapidity until dissolved. Triamylamine hydrochloride also possesses this property in a high degree.

The *platinochloride* crystallises easily in prisms; it is soluble in alcohol, insoluble in water. An estimation of platinum gave: Pt 26·84. Calculated 27·16.

The *aurochloride* crystallises in flattened needles soluble in alcohol, insoluble in water.

Inactive tri-amylamine obtained by fractional distillation, or from the hydrochloride separated from di-amylamine hydrochloride by means of ether, boiled at 237° (uncorr.). It is an oily liquid of sp. gr. 0·7882 at 13°.

The *hydrochloride* crystallises from ether in pearly scales, from water in prismatic needles.

An analysis gave: Cl 13·1. Calculated 13·34. It is soluble in alcohol and ether, less so in cold water.

The *platinochloride* is insoluble in water, soluble in alcohol. An analysis gave: Pt 22·8. Calculated 22·78.

The *aurochloride* crystallises from dilute alcohol in prismatic needles. It is insoluble in water.

Active Amylamines.

From a number of samples of crude amyl alcohol I selected one, which possessed a rotatory power of 1° 30′ for 10 cm., and yielded on

rectification pure amyl alcohol rotating 2° 10′ for the same length. B. p. 127—131°. 3200 grams of this alcohol were distilled in a current of hydrochloric acid in an apparatus consisting of two flasks of 10 litres capacity, so arranged that as soon as all the liquid had distilled from one into the other, it could be made to return by atmospheric pressure. In the second flask was fitted a five-bulb fractionating-tube of Le Bel and Henninger, and the distillation so conducted that the amyl chloride formed just dripped from the condenser attached. In this way the chloride was removed as soon as formed in the receiver, floated on the top of the accompanying amyl alcohol and water. From time to time the chloride was separated, and the lower layer dried and put back into the flask. Even with this apparatus of Le Bel the etherification is slow, and about five weeks were necessary to reduce the quantity of alcohol employed to 760 grams. At this point the distillation was stopped, and the remaining alcohol when dried and distilled, was found to rotate 4° in a tube 10 cm. long.

The mono-amylamine was obtained from this alcohol partly by converting it into cyanate and cyanurate of amyl, and boiling the mixture with potash, and partly, by means of the bromide which, heated to 100° with a large excess of alcoholic ammonia, yielded chiefly amylamine, together with diamylamine in smaller quantity, and traces of triamylamine. That obtained by the latter method, from a bromide rotating 3° to the right, for a length of 10 cm., was somewhat more active than that prepared from the cyanate, and rotated 3° 30′ to the left, while amylamine obtained from the cyanate rotated 3° 5′. Possibly this difference is to be ascribed to the high temperature requisite to distil the mixture of amyl sulphate and cyanate of potassium.

The boiling point of the active amine, after repeated distillation over potash, and finally over sodium, was found to be 96—97°. Its specific gravity at 0° was 0·7725.

It yielded a very deliquescent *hydrochloride*, which gave on analysis Cl 29·00; calculated 28·74. In aqueous solution the hydrochloride rotates feebly to the right. A very concentrated solution obtained by neutralising the base with hydrochloric acid, rotating 0° 30′ for a length of 15 cm.

The *platinochloride* crystallised from hot water in brilliant scales, which closely resembled those of the platinochloride of the inactive amylamine. An analysis gave: Pt 33·63. Calculated 33·73.

At 14° 100 parts of water dissolve 2·4 parts of the salt, which is therefore more soluble than the inactive (1·7 parts). It is nearly insoluble in alcohol.

The *aurochloride* crystallises from dilute alcohol on slow evaporation

in well-defined crystals, presenting the form of a rhomb with one of its acute angles truncated. It is soluble in alcohol.

The active *diamylamine* was obtained in larger quantity by heating the active amyl bromide already described with its own weight of alcoholic ammonia to 130°, whereby chiefly diamylamine was produced. By several fractionations, conversion into its hydrochloride to separate possible traces of amyl alcohol, and distillation over potash, it was obtained boiling at 182—184° (uncorr.), whereas a sample of pure inactive diamylamine, distilled in the same vessel and with the same thermometer, passed over at 186—187°. The specific gravity was found to be the same as that of the inactive amine, 0·7878 at 0°. It rotated 5° 15′ to the *right* for a length of 10 cm.

The *hydrochloride* was obtained as a glassy mass easily soluble in water, alcohol, and ether. It is distinguished from the corresponding inactive salt by its form and by its much greater solubility in cold water. Further by its solubility in ether, in which the inactive salt is quite insoluble. A solution in water containing 0·07836 gram for 1 gram of solution rotated 1° to the right for 10 cm. from which $[\alpha] = 12{\cdot}7$ (neglecting the sp. gr.).

The hydrochloride is therefore more active than the free amine. An analysis gave: Cl = 18·20. Calculated 18·35.

The *platinochloride* is soluble in alcohol, but only slightly soluble in water. Its solution in dilute alcohol deposits large ill-defined tabular crystals on the surface of the liquid, underneath small octohedrons, which do not appear to belong to the cubic system.

The *aurochloride* is insoluble in water, soluble in alcohol; it separates as a yellow amorphous precipitate on addition of solution of gold chloride. From dilute alcohol it separates as a crystalline skin on the surface of the liquid.

The *triamylamine* was obtained by heating the active diamylamine with amyl bromide (3° for 10 cm.) and in the preparation of diamylamine.

It passed over at 230—237° (uncorr.). The sp. gr. at 13° was found to be 0·7964.

The *triamylamine* is remarkably dextrogyrate. I prepared two specimens, of which the one rotated 44° 15′, and the other 44° to the right in a tube 10 cm. long.

The *hydrochloride* was obtained as a syrup, which solidifies when placed over sulphuric acid. Its aqueous solution rotates strongly to the right.

The *platinochloride* is insoluble in water, soluble in alcohol. An estimation of platinum gave: Pt = 23·00. Calculated 22·78.

The *aurochloride* crystallises from dilute alcohol in needles, soluble in alcohol, insoluble in water.

From the above it will be seen that the salts of the active amylamines differ from their inactive isomerides in being deliquescent and difficult to crystallise, and further in their solubility. It was a similar difference in the barium salts of the two varieties of valerianic acid which first led Erlenmeyer to regard the latter as two distinct acids.

The properties already ascribed to the amylamines of their salts naturally agree as a rule with those of the inactive, rather than with those of the active compounds, inasmuch as ordinary amyl alcohol usually contains only about 15 per cent. of the active alcohol.

It cannot be claimed for the active amines here described, that they are absolutely pure, for neither the process of Le Bel nor that of Pasteur appear to allow of a complete separation of the alcohols; the alcohol employed possessed, however, nearly the maximum rotation observed.

The polariscope used in these experiments was that of Cornu, and the rotation is given for the yellow ray.

In conclusion, I have to add that this investigation was carried out in the laboratory of Professor Wurtz, in Paris.

XLVIII.—*On the Products of the Action of Alkalis on Ethylic β-ethylaceto-succinate.*

By L. T. Thorne, Ph.D. (late Jodrell Scholar).

Ethylic β-ethylaceto-succinate was first prepared by Clowes in 1875 (*Ber.*, **8**, 1208), but owing to the difficulty of the methods of preparation then in use, he was only able to obtain the ether in very small quantities. The notice above cited contains in fact little more than the boiling point of the ether and its capability of dissolving sodium with evolution of hydrogen, whereas ethylic α-ethylaceto-succinate (Huggenburg, *Ann. Chem.*, **192**, 146) is not acted on by sodium at ordinary temperatures. As it was of interest to examine the action of alkalis on this ether, I undertook, at the suggestion of Prof. Wislicenus, its preparation in larger quantities, and its closer examination.

According to the researches of Wislicenus (*Ann. Chem.*, **186**, 221), the decomposition, under these circumstances, should take place according to the two following equations:—

I. $CO_2Et.CH\bar{A}c.CHEt.CO_2Et + 3KOH = CO_2K.CH_2.CHEt.CO_2K + CH_3.CO_2K + 2EtOH.$

II. $CO_2Et.CH\bar{A}c.CHEt.CO_2Et + 3KOH = CH_2\bar{A}c.CHEt.CO_2K + K_2CO_3 + 2EtOH.$

This expectation was justified, as in every case the two processes went on side by side, their quantitative relations depending on he strength of the alkaline solution used. A strong aqueous solution of caustic potash splits up the ether, principally according to equation I, a dilute aqueous or alcoholic, according to II.

In the preparation of ethylic β-ethylaceto-succinate, Conrad and Limpach's improved method (*Ann. Chem.*, **192**, 153) for the formation of derivatives of ethylic aceto-acetate was used. 12 grams sodium were dissolved in 120 grams absolute alcohol and 68 grams ethylic aceto-acetate added to the cooled liquid; 102 grams ethylic α-brom-butyrate were then gradually introduced, the whole being constantly agitated. After heating the mixture in a retort with inverted condenser on the water-bath until it became neutral, the alcohol was distilled off, and the residual liquid washed, dried, and distilled. The pure ether boils at 263°, and distils under ordinary atmospheric pressure without decomposition; but I found that by far the best yield of substance was obtained when the fractional distillation was carried out under reduced pressure—a pressure of 60—80 mm. mercury was used.

Ethylic β-ethylaceto-succinate is a colourless oily liquid of pleasant odour, which somewhat resembles that of ethylic aceto-acetate. It boils at 263°, and its sp. gr. is 1·064 at 16° C., compared with water at 17·5°. It is miscible in all proportions in alcohol and ether, insoluble in water. Its analysis gave the following numbers:—

I. 0·2241 gram ether gave 0·1634 gram H_2O and 0·4802 gram CO_2.
II. 0·1600 gram ether gave 0·1137 gram H_2O and 0·3430 gram CO_2.

	Theory.			Found.	
				I.	II.
C_{12}	= 144	=	59·01	58·44	58·53
H_{20}	= 20	=	8·19	8·10	7·89
O_3	= 80	=	32·79	—	—

Before commencing the study of the saponification-products of this ether, I made experiments to determine the quantitative relations in which the two above-mentioned reactions take place. The determinations were made in the way described by Wislicenus (*Ann. Chem.*, **190**, 257, and **206**, 308). The alcoholic potash solutions used had the strength of 21·672 per cent. and 10·836 per cent. KOH respectively. The results are given in the following table, the numbers being in each case the mean of two closely agreeing determinations:—

		I. 21·672 per cent. potash solution.	II. 10·836 per cent. potash solution.
1.	Ether used	2·44 grams	2·44 grams
2.	KOH „	2·514 „	2·514 „
3.	CO_2 formed	0·2162 „	0·2725 „
4.	KOH, free and as K_2CO_3	1·5890 „	1·7290 „
3.	KOH as salts of the three acids	0·9250 „	0·7850 „
4.	KOH as $K.C_2H_3O_2$ and $K_2.C_6H_8O_4$	0·6497 „	0·4381 „
5.	KOH as $K.C_7H_{11}O_3$	0·2752 „	0·3469 „
6.	Ether split up according to equation I	0·9400 „	0·6365 „
7.	Ether split up according to equation II	1·1978 „	1·5105 „
	Ether decomposed	2·1378 „	2·1470 „
8.	Per cent. of ether decomposed	87·62 p. c.	88·02 p. c.
	a. in $C_6H_{10}O_2$ and $C_2H_4O_2$	38·53 „	26·10 „
	b. in $C_7H_{12}O_3$ and CO_3	49·09 „	61·92 „

From these numbers it is seen that the decomposition of ethylic β-ethylaceto-succinate agrees closely with that of the hitherto observed derivatives of ethylic aceto-acetate, the quantity of ether split up into the ketonic acid diminishing as the strength of the caustic potash solution employed is greater.

As I wished to establish the identity of the ethyl-succinic acid obtained from this ether with that which Huggenburg (*Ann. Chem.*, **192**, 146) obtained from ethylic α-ethylaceto-succinate, I used, in my early experiments, a very concentrated solution of potassic hydrate. About five times the theoretically requisite quantity of KOH was dissolved in about half its weight of water. The thick oily liquid thus obtained (it is solid below 50—60° C.), was heated in a silver crucible on a water-bath, and the ether introduced drop by drop, the liquid being constantly stirred. Each drop of ether was instantly decomposed, and I found that under these conditions almost the whole of the ether split up into ethyl-succinic and acetic acids. After completion of the reaction, the whole was dissolved in water, neutralised, and any traces of undecomposed ether extracted with ether. Sulphuric acid was then added in excess, and the organic acids were shaken out with ether. The etheric solution left, on evaporation, a thick brown syrup, which solidified on standing under the receiver of the air-pump. In order to obtain the ethyl-succinic acid pure, I pursued the following plan: The crystalline mass which contained ethyl-succinic, acetic, and α-ethyl-β-aceto-propionic acids, was dissolved in water and boiled with barium carbonate. The solution of barium salts thus obtained was mixed with about half its volume of alcohol. A yellowish precipitate

was thus formed, consisting principally of barium ethyl-succinate. After repeated solution and reprecipitation, a tolerably white powder was obtained, which, however, proved, on analysis, to be still far from pure. It was then redissolved in water, the barium exactly precipitated with sulphuric acid, and the filtrate evaporated. The crystalline acid thus obtained was pressed between filter-paper, and several times recrystallised from ether and water; but as it proved still impure, was next converted into the calcium salt, which is much more easily soluble in hot than in cold water, and should therefore give a good means of purifying the acid. I found, however, that although calcium α-ethyl-β-aceto-propionate is in itself very soluble in water, it still adheres very obstinately to the calcium ethyl-succinate, and it was only after recrystallising upwards of 40 times that I obtained the latter salt approximately pure. The calcium ethyl-succinate thus obtained gave the following analytical results:—0·4315 gram salt heated to 150° C. for some time, lost 0·0714 gram in weight. This is equivalent to 16·52 per cent. water of crystallisation, Huggenburg's salt, $Ca.C_6H_8O_4 + 2H_2O$, requiring 16·41 per cent.

I. 0·1485 anhydrous salt gave 0·0596 gram H_2O, 0·2101 gram CO_2, and 0·0440 gram CaO.

II. 0·1501 anhydrous salts gave 0·0570 gram H_2O, 0·2141 gram CO_2, and 0·0453 gram CaO.

	Theory.			Found.	
				I.	II.
C_6	= 72	=	39·13	38·57	38·90
H_8	= 8	=	4·35	4·46	4·22
O_4	= 64	=	34·78	—	—
Ca	= 40	=	21·74	21·23	21·56

The free acid was obtained from the Ca salt by solution in water, acidifying with H_2SO_4, and extraction with ether. After recrystallisation it showed the melting point 98°, given by Huggenburg, and gave satisfactory numbers on analysis.

0·1830 gram acid gave 0·1107 gram H_2O and 0·3287 gram CO_2.

	Theory.			Found.
C_6	= 72	=	49·31	48·98
H_{10}	= 10	=	6·85	6·72
O_4	= 64	=	43·84	—

Thus, as was to be expected, the ethyl-succinic acids obtained from α- and from β-ethylaceto-succinic ether are identical.

I now turned my attention to the second reaction, and here, following the indications of the before-mentioned quantitative determinations, I used a very weak caustic potash-solution as decomposing

medium. In the first place, however, I tried the action of sulphuric and hydrochloric acids, as in many of the ethylic aceto-acetate derivatives these acids cause the decomposition almost entirely into ketone and carbonic anhydride. 2·0605 grams ethylic β-ethylaceto-succinate were heated with excess of dilute sulphuric acid, and the evolved CO_2 passed into barium hydrate solution. By the time the reaction was completed, barium carbonate, equivalent to 0·30683 gram CO_2, had been precipitated. This represents 82·59 per cent. of the ether decomposed into ketonic acid and CO_2. Notwithstanding this apparently favourable result, I found this method unsuitable in practice, as secondary resinous products were formed, which rendered the purification much more difficult. I therefore employed a 5 per cent. solution of potassium hydrate, taking only a very slight excess (about a fourth more than theoretically required). After boiling for some hours the whole of the ether disappeared, and the liquid was evaporated to a smaller bulk, acidulated with excess of H_2SO_4, and the liberated organic acid extracted with ether. After distilling off the ether the acid remained behind as a thick brownish fluid. Subjected to *rapid* distillation, the greater part passed over between 245° and 252°, and gave the following numbers on analysis:—

I. 0·1830 gram acid gave 0·1335 gram H_2O, and 0·3902 gram CO_2.
II. 0·1021 „ „ 0·0756 „ H_2O, and 0·2170 „ CO_2.

	Calculated for $C_7H_{12}O_3$.	Found. I.	Found. II.
C	= 58·33	58·15	57·96
H	= 8·33	8·10	8·22
O_3	= 33·33	—	—

The acid is, therefore, undoubtedly α-ethyl-β-aceto-propionic acid. Thus obtained, this acid is a colourless liquid, which rapidly turns brown on exposure to the air. It has a sweetish odour and strongly acid taste and reaction. It boils apparently between 250° and 252°, and does not solidify even at −15°. It is miscible in all proportions with water, alcohol, and ether.

On submitting it to fractional distillation, with the view of purifying it, the various fractions all gave analytical results less in accordance with theory than the above. I found that the percentage of carbon increased, that of hydrogen decreased each time the acid was distilled. The following are a few of the analyses of different fractions:—

	I.	II.	III.	IV.	V.	VI.
C	58·86	58·78	59·19	59·26	59·28	59·51
H	8·26	8·04	8·03	8·10	8·09	8·10

At the same time I observed that traces of water always made their appearance during the refractioning of the acid. I therefore examined the distillate, and found it to be no longer completely soluble in water, a small quantity of an oily liquid always remaining undissolved. This liquid was separated from the aqueous solution of the acid, shaken with aqueous potassium carbonate, and dried over the fused salt. On distillation, almost the whole passed over between 218° and 222°. Refractioned, fraction 219° and 220° gave the following numbers:—

I. 0·1324 gram substance gave 0·0968 gram H_2O and 0·3225 gram CO_2.

II. 0·1467 gram substance gave 0·1058 gram H_2O and 0·3577 gram CO_2.

	I.	II.
C	= 66·43	66·50
H	= 8·12	8·01

These numbers agree very closely with those required for the acid, less the elements of water. $C_7H_{12}O_3 - H_2O = C_7H_{10}O_2$.

C_7	= 84	= 66·66
H_{10}	= 10	= 7·94
O_2	= 32	= 25·40

It follows therefore that, on distillation, α-ethyl-β-aceto-propionic acid splits up into water and this new substance. A few preliminary experiments with the latter are described at the close of this paper.

All endeavours to obtain the ketonic acid pure proved fruitless, and no more success was met with in the attempt to prepare its salts. All its salts are soluble in water, and on evaporation are left behind as uncrystallisable gum-like masses, from which no satisfactory analysis could be obtained. In very concentrated neutral solutions silver nitrate gives a white precipitate, but as both precipitate and solution decompose rapidly even in the dark, this salt could not be obtained in a pure state.

The only derivative of the acid which I succeeded in purifying was the ether. This was made by heating the dried but *undistilled* acid with absolute alcohol and a few drops of H_2SO_4. Ethylic α-ethyl-β-aceto-propionate is a colourless oily liquid, boiling at 224—226°. It is lighter than water, soluble in ether and alcohol, insoluble in water.

I. 0·1198 gram ether gave on analysis 0·0985 gram H_2O and 0·2755 gram CO_2.

II. 0·1440 gram ether gave on analysis 0·1229 gram H_2O and 0·3300 gram CO_2.

	Theory.		Found.	
C_9	= 108	= 62·79	62·71	62·50
H_{16}.....	= 16	= 9·30	9·14	9·48
O_3	= 48	= 27·31	—	—

In order further to characterise the acid, I determined to examine its oxidation-products. According to analogy, α-ethyl-β-aceto-propionic acid on oxidation should produce ethyl succinic acid according to the equation—

$$\begin{array}{l}CH_2.CO.CH_3\\ |\\ CH.CH_2.CH_3\\ |\\ COOH\end{array} + 2O_2 = \begin{array}{l}COOH\\ |\\ CH\\ |\\ CH.CH_2CH_3\\ |\\ COOH\end{array} + CO_2 + H_2O,$$

and this reaction would serve instead of salts as a means of identification.

Small quantities of acid were introduced into porcelain crucibles, a large excess of dilute nitric acid was added, and the whole heated on a water-bath. The action began in a very short time, CO_2 and nitric fumes being copiously evolved. The solution was then evaporated to dryness, the treatment with dilute nitric acid repeated several times, and finally the residue evaporated two or three times with water to get rid of excess of nitric acid. The crystalline acid thus obtained was converted into the calcium salt, and the latter purified by oft-repeated crystallisations.

0·3863 gram Ca salt lost at 150° C 0·0630 gram H_2O, equivalent to 16·31 per cent.; $CaC_6H_8O_4 + 2H_2O$ requires 16·41 per cent.

0·1651 gram dried salt gave 0·0667 gram H_2O, 0·2346 gram CO_2, and 0·0500 gram CaO.

	Theory.		Found.
C	=	39·13	38·75
H	=	4·35	4·37
Ca.....	=	21·74	21·63
O	=	34·78	—

The free acid was also prepared from the calcium salt, and after recrystallisation showed the fusing point 98° C.

Thus it is clear, both from its formation and also from its oxidation-products, that the substance under consideration is *α-ethyl-β-aceto-propionic acid*, $CH_3.CO.CH_2.CH(C_2H_5).COOH$, a homologue of the four* ketonic acids hitherto known.

* Since the above was written, Pinner (*Ber.*, **14**, 1073) has described the isomeride, α-dimethyl-β-acetopropionic acid, $CH_2Ac.CM_2.CO_2H$.

Preliminary Examination of the Substance obtained during the Distillation of α-Ethyl-β-aceto-propionic Acid.

This substance, already mentioned, was prepared in somewhat larger quantities as follows. The ketonic acid was introduced into a fractioning flask, and heated till the liquid attained a temperature of about 230°, and just began to boil. Just sufficient heat was applied to distil over the water formed, while any vapour of the new substance recondensed on the cooler parts of the flask. As soon as the water ceased to be formed, the residue was further heated, when the greater part boiled between 225° and 235°. This was then purified as already described.

This substance when pure is a colourless oily liquid of pleasant odour and neutral reaction. Its boiling point is 219°, and its sp. gr. 1·0224 at 20°, compared with water at the same temperature. It is soluble in alcohol and ether, insoluble in water. Its dispersive power and index of refraction were determined by means of Abbe's refractometer as follows :—

Dispersive power between D and F lines.....	0·0071
Index of refraction for D line	1·4554

Its vapour-density determined by Dumas' method gave 5·014 (air = 1), whilst the formula $C_7H_{10}O_2$ would require 4·363. Although, owing to the small quantity of substance at my disposal, these figures are not as satisfactory as were desirable, still when the low boiling point of the substance is considered, they leave little room for doubt that the molecular formula is $C_7H_{10}O_2$, and not a multiple thereof.

This substance can be shaken and even heated with water without change, but when boiled with a solution of caustic soda, it is slowly dissolved. On using a titrated solution of soda, I found that exactly 1 mol. of NaOH was neutralised by each molecule of the substance, but I cannot at present say with certainty whether the ketonic acid was reproduced, or whether further decomposition took place.

The formation of this substance is undoubtedly expressed by the equation—

$$CH_3.CO.CH(C_2H_5).CH_2.CO_2H = C_7H_{10}O_2 + H_2O,$$

but where the separation of the elements of water takes place must remain at present an open question. I hope shortly to continue the study of this and similar bodies, and therefore propose to leave it unnamed until I am in possession of more information concerning its constitution.

In conclusion, I wish to express my sincere thanks to Professor J. Wislicenus for the valuable assistance and advice so kindly vouchsafed

to me during the progress of the preceding research; and also to Professor M. Nencki for his courtesy in placing his laboratory in Bern at my disposal, and thus enabling me to complete the latter part of this work during my absence from Würzburg.

XLIX.—*On the Action of Sodium Alcoholates on Fumaric Ethers.*

By T. Purdie, B.Sc., Ph.D.

It is well known that in aceto-acetic ether, in malonic ether, and in the nitroparaffins, atoms of hydrogen, which are directly united with a particular atom of carbon, may be replaced by atoms of strongly positive metals. This property seems to depend on the presence of electronegative atoms or radicals, which are combined with the carbon-atom in question. It is also a well-known fact that a relatively electronegative character is imparted to a hydrocarbon group, if one or more double or triple bonds between carbon-atoms occur in the molecule; the general behaviour of many benzene derivatives, and the replaceability of an atom of hydrogen by sodium in acetylene and its homologues may be cited as examples in point.

It seemed not improbable that similar relations might be found to exist in the ethers of the unsaturated acids; that, for example, in the case of fumaric ether, the combined influence of the double bond, and the proximity of the carboxyl groups might so weaken the force with which the hydrogen atoms of the —CH = CH— group are bound, that one or both of them might be replaced by sodium. It would then be possible by the action of haloïd ethers on the sodium-compound to effect a direct synthesis of the homologues of fumaric acid.

Professor Wislicenus, in whose laboratory and under whose direction the following research was conducted, had already investigated the action of the alkali-metals on ethyl fumarate. Sodium exerted little or no action at the ordinary temperature; potassium acted vigorously, but the product was of such a complicated nature as to offer little prospect of a satisfactory elucidation of the reaction. More recently, on the other hand, by the action of sodium ethylate in alcoholic solution and subsequent addition of methyl iodide, according to the method practised in the University Laboratory at Würzburg in the aceto-acetic ether syntheses, Wislicenus had obtained a dibasic acid, the composition of which, according to the analyses of the barium and the silver salt, corresponded with the formula $C_6H_{10}O_5$. A saturated

addition product had evidently been formed, probably, as it seemed, a dimethylmalic acid of the formula $CH_3.C(OH)(CO_2H).CH(CO_2H).CH_3$. In this experiment sodium ethylate, ethyl fumarate, and methyl iodide had been employed in the proportions of their molecular weights, and monomethylfumaric acid was expected as the probable product of the reaction. The simultaneous substitution of two atoms of hydrogen by methyl-groups seemed easily explained on the ground of the symmetrical structure of the fumaric ether.

The presence of a large quantity of unaltered fumaric ether in the product of the reaction confirmed the supposition. Besides this the solubility of the barium salt indicated that the acid was a hydroxy acid. According to this hypothesis, the element of a molecule of water had been added by a secondary reaction during the saponification, and a saturated acid formed. It was, however, possible that the methyl-radical did not enter at all into the constitution of the acid, but that the elements of a molecule of ethylic alcohol had been added to the fumaric acid, and an ethyl-malic acid formed.

The reaction might then be expressed as follows :—

$$\begin{array}{l} CH.COOC_2H_5 \\ \| \\ CH.COOC_2H_5 \end{array} + C_2H_5ONa = \begin{array}{l} CH.Na.COOC_2H_5 \\ | \\ CH(OC_2H_5)COOC_2H_5 \end{array}$$

$$\begin{array}{l} CH.Na.COOC_2H_5 \\ | \\ CH(OC_2H_5)COOC_2H_5 \end{array} + CH_3I + C_2H_5OH = \begin{array}{l} CH_2.COOC_2H_5 \\ | \\ CH(OC_2H_5)COOC_2H_5 \end{array} + CH_3OC_2H_5 + NaI;$$

or

$$\begin{array}{l} CH.COOC_2H_5 \\ \| \\ CH.COOC_2H_5 \end{array} + C_2H_5ONa = \begin{array}{l} CH.ONa.COOC_2H_5 \\ | \\ CH.(C_2H_5)COOC_2H_5 \end{array}$$

$$\begin{array}{l} CH.ONa.COOC_2H_5 \\ | \\ CH(C_2H_5)COOC_2H_5 \end{array} + CH_3I + C_2H_5OH = \begin{array}{l} CH.OH.COOC_2H_5 \\ | \\ CH(C_2H_5)COOC_2H_5 \end{array} + CH_3OC_2H_5 + NaI.$$

In either case only the basic ethoxyl-groups would of course be replaced by hydroxyl by the saponification. The following experiments were undertaken, at the suggestion of Professor Wislicenus, in order to determine the constitution of the acid and the mode of its formation.

Preparation of the Fumaric Acid.

The fumaric acid was prepared in the usual manner from malic acid. The malic acid was heated slowly in a current of air to 150°,

and finally to 180°, as long as water and maleic acid distilled over. The solid residue was powdered, washed with small quantities of cold water, and dried at 100°. The yield in three different experiments, 250 grams of malic acid being used each time, was 169 grams, 154 grams, and 170 grams of fumaric acid.

Preparation of Ethyl Fumarate.

The ethylic ether was prepared from the acid in three different ways, namely: by passing hydrochloric acid gas into a mixture of alcohol and acid; by heating the acid with sulphuric acid and alcohol; and by the action of silver fumarate on ethyl iodide.

The first of these methods, which is the one most frequently employed for the preparation of the ether, is coupled with certain disadvantages. Owing to the slight solubility of fumaric acid in alcohol in the cold, it is necessary to conduct the operation over the water-bath, and at this temperature much chlorosuccinic ether is formed. The decomposition of the latter is effected only after often repeated distillation, and entails a loss of ether due to saponification by the evolved hydrochloric acid gas.

The following may serve as an example of the second method of preparation: To 149 grams of fumaric acid were added 450 grams of absolute alcohol, and 15 grams of concentrated sulphuric acid, and the mixture was heated for four hours over the water-bath. On cooling, water was added, and the oily layer was separated, washed with water, and dried with calcium chloride. The wash-water was shaken up with ether, and the fumaric ether thus extracted added to the main portion. After distilling twice, the portion between 213° and 220°, which was used for part of the experiments described below, amounted to 123 grams. The actual boiling point of ethyl fumarate is 218° (*Jahresb.*, 1872, 515; *Ber.*, 1879, 2282). In the preparation of the ether from the silver salt, the following method was pursued: Silver fumarate precipitated with silver nitrate from the solution of ammonium fumarate was dried at 80°, 81 grams of the dried salt were added gradually to 100 grams of ethyl iodide in a retort fitted with inverted condenser, the retort being gently heated until action set in. When the violent action had ceased, ether was added, and the mixture heated over the water-bath. The liquid was then filtered off, the silver iodide washed with ether, and the residue after distilling off the ether fractionated. The portion boiling at 214—216° (not corrected) amounted to 17 grams, and was found by the following analysis to be pure.

0·2320 gram of the substance yielded on combustion 0·1471 gram of water, and 0·4725 gram of carbonic anhydride.

	Calculated for $C_8H_{12}O_4$.	Found.
Carbon	55·81	55·54
Hydrogen	6·98	7·05
Oxygen	37·21	—
	100·00	

Action of Sodium Ethylate and Methyl Iodide on Ethyl Fumarate.

This operation was conducted according to the method used in the Würzburg Laboratory in the preparation of the organic disubstituted aceto-acetic ethers, which, as it has been frequently described (*Annalen*, **192**, 153), it is unnecessary to treat in detail. In the first experiment the ingredients were used in the proportion of 2 mols. of methyl iodide to 2 atoms of sodium, and 1 mol. of ethyl fumarate. On adding the first half of the sodium ethylate, a yellow precipitate is formed with evolution of heat, and also on addition of the methyl iodide, considerable heating takes place. The mixture was heated over the water-bath for half an hour, after which it was neutral to test-paper; the alcohol was then distilled off, and water added to the residue. No oil separated; by shaking with ether, a small quantity was extracted from the aqueous solution, which, however, on saponification and decomposition of a lead salt procured from it, yielded only hydriodic and fumaric acids. The aqueous solution from which this oil was extracted was then examined. On evaporating, besides sodium iodide and a smeary substance, an organic sodium salt separated out. As the latter could not be procured pure, the calcium salt was precipitated with calcium chloride. The difficultly soluble crystalline precipitate was filtered off, pressed between filter-paper, and then dissolved in a large quantity of water. The solution yielded on evaporation a crystalline powder, which, after being washed with alcohol and dried *in vacuo*, gave on analysis the following numbers:—

0·1860 gram of the substance yielded 0·0751 gram H_2O, 0·2469 gram CO_2, and 0·0523 gram CaO.

	Calculated for $C_6H_8CaO_5$.	Found.
Carbon	36·00	36·21
Hydrogen	4·00	4·48
Calcium	20·00	20·09
Oxygen	40·00	—
	100·00	

From the small quantity of oil obtained by extraction, and the occurrence of the above-mentioned sodium salt in the aqueous solution, it was concluded that the ether, which was probably formed, had been

saponified by the excess of sodium ethylate. In the next experiment, therefore, only half as much sodium and methyl iodide were used as is required by the proportions already mentioned. The mixture showed a neutral reaction after being heated for only 20 minutes. On addition of water, much oil remained undissolved, which was separated from the aqueous solution, and treated as is described below. The aqueous solution by extracting with ether yielded an oil, which, after drying with potassium carbonate, boiled above 225°, but as it showed signs of decomposition at this temperature, it was distilled under diminished pressure. On fractioning, the chief portion boiled between 195° and 200° under a pressure of 250 mm., and on analysis proved to be the diethylic ether of the acid of formula $C_6H_{10}O_5$, already referred to, although the calculated composition of this body does not differ so much from that of ethyl fumarate that the purity of the substance can be proved by analysis.

I. 0·2282 gram of the substance gave 0·1713 gram H_2O and 0·4587 gram CO_2.

II. 0·2402 gram of the substance gave 0·1786 gram H_2O and 0·4814 gram CO_2.

Calculated for $C_{10}H_{18}O_5$.		Found. I.	Found. II.
Carbon	55·04	54·82	54·66
Hydrogen	8·26	8·34	8·26
Oxygen	36·70	—	—
	100·00		

The main portion of the oil, which was separated from the aqueous solution, was directly saponified with potassium hydrate, and the solution then neutralised with acetic acid. On addition of neutral, and afterwards of basic lead acetate, only small precipitates were formed, which were filtered off. By adding lead nitrate to the filtrate, after it had been slightly acidulated with nitric acid and then neutralised with ammonia, a heavy crystalline precipitate was formed more quickly on stirring. This lead salt was decomposed with sulphuretted hydrogen, and yielded on evaporation of the aqueous filtrate, and subsequent drying of the residue *in vacuo*, a colourless syrup, which after some days solidified to transparent crystals. The melting point of the acid crystallised from ethereal solution and dried *in vacuo*, was 86°. The analysis gave the following numbers :—

I. 0·3042 gram of the substance gave 0·1705 gram H_2O and 0·4933 gram CO_2.

II. 0·2588 gram of the substance gave 0·1453 gram H_2O and 0·4217 gram CO_2.

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Calculated for $C_6H_{10}O_5$.		Found. I.	Found. II.
Carbon	44·45	44·23	44·44
Hydrogen	6·17	6·23	6·24
Oxygen	49·38	—	—
	100·00		

Action of Sodium Ethylate and Ethyl Iodide on Ethyl Fumarate.

In order to determine whether the acid obtained as above was a dimethylmalic acid, or a product formed by the simple addition of the elements of a molecule of ethylic alcohol, the action of ethyl iodide on a mixture of ethyl fumarate and sodium ethylate was investigated. According to the constitution of the acid there would be formed either a dimethylmalic acid, or the same acid as when methyl iodide is employed. The proportion of ingredients used and the process were the same as in the last experiment. By addition of water to the product of the reaction, an oil and an aqueous solution were obtained. Before saponifying the former, an attempt was made to purify it by distillation, but decomposition took place, and no acid except some fumaric acid could be procured from it. On the other hand, from the aqueous solution containing much sodium iodide, a calcium salt was procured in the form of a crystalline precipitate, which was pressed in filter-paper, washed with alcohol, dissolved again in hydrochloric acid, and by neutralising and boiling again precipitated. It resembled in every respect the calcium salt obtained from the previous experiment, and the analysis of the salt dried *in vacuo* proves that the same acid is formed, no matter whether methyl or ethyl iodide be used.

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I. 0·1906 gram of the substance gave 0·0717 gram H_2O, 0·2506 gram CO_2, and 0·0546 gram CaO and $CaCO_3$; after treatment with ammonium carbonate, 0·0968 gram $CaCO_3$.

II. 0·1880 gram of the substance gave 0·0706 gram H_2O, 0·2498 gram CO_2, and 0·0543 gram CaO and $CaCO_3$; after treatment with ammonium carbonate, 0·0957 gram $CaCO_3$.

Calculated for $C_6H_8CaO_5$.		Found. I.	Found. II.
Carbon	36·00	35·92	36·33
Hydrogen	4·00	4·18	4·17
Calcium	20·00	20·31	20·36
Oxygen	40·00	—	—
	100·00		

Action of Sodium Ethylate on Ethyl Fumarate.

It appeared from the above experiments that the alcohol iodide had taken no part in the formation of the acid, except in so far as it might serve for the decomposition of the sodium compound, which, it was to be presumed, was first formed. Accordingly in the next experiment sodium ethylate, in alcoholic solution as before, was made to act by itself on ethyl fumarate, and in the proportion of 1 atom of sodium to 1 molecule of the ether. To avoid rise of temperature, the ether was gradually added to the sodium ethylate solution, and then after some hours, without heating, simply water was added, in which the product dissolved, without any considerable evolution of heat or any separation of oil, to a reddish-brown neutral liquid. This was heated over the water-bath, and sodium hydrate added, until the solution remained permanently alkaline. After neutralising with acetic acid and distilling off the alcohol, on addition of neutral lead acetate a lead salt was procured, which yielded only fumaric acid. When the solution, freed in this way from fumaric acid, was neutralised with nitric acid, and lead nitrate added, a crystalline insoluble lead salt was obtained. This yielded on decomposition with sulphuretted hydrogen an acid syrup, which solidified on standing to a crystalline mass. The melting point (86°) of the acid, crystallised from ether and dried *in vacuo*, and also its composition, as determined by the following analysis, agreed exactly with those of the acid already described.

0·2127 gram of the substance gave 0·1201 gram H_2O and 0·3467 gram CO_2.

	Calculated for $C_6H_{10}O_5$.	Found.
Carbon	44·45	44·45
Hydrogen	6·17	6·27
Oxygen	49·38	—

It was afterwards found that the ethyl fumarate which had been employed in the experiments in which the acid was obtained in the free state, was contaminated with a substance containing chlorine, probably with ethyl chlorosuccinate. It is evident that this ether, by double decomposition with sodium ethylate, would yield an ethyl malic acid. The ethyl fumarate used in the other experiments was prepared by the sulphuric acid method, and it is scarcely possible that it could contain an addition-product corresponding to the ethyl chlorosuccinate. The reaction with sodium ethylate was, nevertheless, repeated on pure ethyl fumarate prepared from the silver salt, the analysis of which has already been given. The same acid, melting at 86°, was obtained, as is seen from the following analysis:—

0·2345 gram of the substance gave 0·1310 gram H_2O and 0·3813 gram CO_2.

	Calculated for $C_6H_{10}O_5$.	Found.
Carbon	44·45	44·35
Hydrogen	6·17	6 21
Oxygen	49·38	
	100·00	

From 5 grams of ethyl fumarate, 2 grams of the new acid were obtained.

It appears from this experiment that the acid in question is produced by the addition of the elements of a molecule of ethyl alcohol to fumaric acid, but this, as already mentioned, could take place in two different ways. According as the oxygen on the splitting up of the sodium ethylate remains in combination with the ethyl-group or with the sodium, there will result, as a final product, when the atom of sodium is replaced by hydrogen, either ethyl ether malic acid, or ethylmalic acid proper. To determine which of these two had been formed, the substance was heated with fuming hydriodic acid. The reduction products of the first must be ethyl iodide and succinic acid, that of the second ethyl-succinic acid. 0·7 gram of the acid was heated to 120° for three hours in a closed tube with fuming hydriodic acid. On distilling off the latter a few drops of oil first passed over, which, judging from its smell, consisted of ethyl iodide. From the crystalline residue, which was mixed with much free iodine, 0·15 gram of a pure product was obtained, which agreed exactly in its properties with succinic acid. Inhalation of its vapour produced the characteristic irritation, the acid neutralised with ammonia, gave with ferric chloride a brown, and with baric chloride, on addition of alcohol, a white precipitate.

The acid melted at 180°, and on analysis gave the following results:—

0·1053 gram of the substance gave 0·0499 gram H_2O and 0·1572 gram CO_2.

	Calculated for $C_4H_6O_4$.	Found.
Carbon	40·68	40·71
Hydrogen	5·08	5·27
Oxygen	54·24	—
	100·00	

The acid in question is therefore an ethyl ether malic acid of the

formula $\begin{matrix}CH(OC_2H_5)COOH\\ |\\ CH_2.COOH\end{matrix}$, isomeric with the monethyl malate obtained by Demondesir in preparing diethyl malate (*Jahresb.*, 1851, 514). It is readily soluble in water and in ether, and by evaporation of the solvent is obtained as a thick syrup, which crystallises on standing in crystals apparently rhombic. With basic lead acetate it is not precipitated; in neutral and in weakly acid solution, however, it is precipitated by lead nitrate; neutral acetate also causes precipitation, but less quickly. Besides the already mentioned anhydrous insoluble calcium salt, the silver and barium salts were also analysed. The silver salt was prepared by precipitating with silver nitrate from the aqueous solution of the ammonium salt (in combustion I), and from that of the barium salt (in combustion II). It forms a flocculent, on standing somewhat granular precipitate, little soluble in water, and, when dry and protected from light, tolerably stable.

The analysis of the salt, dried *in vacuo*, gave the following numbers:—

I. 0·2468 gram gave 0·0498 gram H_2O, 0·1752 gram CO_2, and 0·1414 gram Ag.

II. 0·2690 gram gave 0·0543 gram H_2O, 0·1915 gram CO_2, and 0·1536 gram Ag.

		Found.	
Calculated for $C_6H_8Ag_2O_5$.		I.	II.
Carbon	19·15	19·36	19·42
Hydrogen	2·13	2·24	2·24
Silver	57·45	57·29	57·10
Oxygen	21·27	—	—
	100·00		

The barium salt, obtained by neutralising the aqueous solution of the acid with barium hydrate, and evaporation over sulphuric acid, forms a powder consisting of microscopic prisms, readily soluble in water. The salt contains apparently a molecule of water of crystallisation, which is given off partly by standing over sulphuric acid, but completely only by heating to 160°. As the salt is also extremely hygroscopic, no satisfactory determination of the water of crystallisation could be obtained.

I. 0·2773 gram of the salt, dried over sulphuric acid, lost, when heated to 160°, 0·0139 gram H_2O; 0·2557 gram of the salt, dried at 160°, gave on combustion 0·0642 gram H_2O, 0·1843 gram CO_2; and from the residue 0·2004 gram $BaSO_4$, corresponding to 0·0378 gram CO_2 and 0·1178 gram Ba.

II. 0·2665 gram of the substance (dried at 160°) gave 0·0660 gram H_2O, 0·1985 gram CO_2, and 0·1767 gram $BaCO_3$, corresponding to 0·0395 gram CO_2, and 0·12288 gram Ba.

III. 0·3629 gram of the substance (dried at 160°) gave 0·0892 gram H_2O, 0·2695 gram CO_2, and 0·2412 gram $BaCO_3$, corresponding to 0·0539 gram CO_2, and 0·16774 gram Ba.

Calculated for $C_6H_8BaO_5 + H_2O$.		Found. I.
Carbon	22·86	22·51
Hydrogen	2·54	2·65
Barium	43·49	43·77
Oxygen	25·40	—
Water	5·71	5·01
	100·00	

Calculated for $C_6H_8BaO_5$.		Found. II.	Found. III.
Carbon	24·24	24·35	24·30
Hydrogen	2·69	2·75	2·73
Barium	46·13	46·11	46·22
Oxygen	26·94	—	—
	100·00		

Action of Sodium Isobutylate on Isobutyl Fumarate.

That ethyl fumarate should form addition compounds with great ease on treatment with bromine or hydrobromic acid is not surprising. R. Anschütz (*Ber.*, 1879, 2282) has in fact found that this ether takes up bromine as easily as any known compound of maleic acid. It is, however, rather remarkable that a substance of this nature should effect the splitting up of sodium ethylate. It seemed, therefore, desirable to ascertain if the reaction were general, and for this purpose the action of sodium isobutylate was investigated. This homologue was chosen in preference to sodium methylate, partly because it is more readily decomposed than the latter, partly because the isobutyl fumarate, which must be used in the reaction instead of the ethyl ether, has not as yet been prepared.

By the action of hydrochloric acid on fumaric acid and isobutylic alcohol, the isobutyl fumarate was not procured free of chlorine compound. Fumaric acid in contact with isobutylic alcohol, which is saturated with hydrochloric acid gas, is but sparingly dissolved in the cold; at 100° etherification is quickly effected. The oil, separating on addition of water, dried with potassium carbonate, boiled after dis-

tilling off the excess of alcohol at 265—270°. It contained, however, even after prolonged heating to 220°, while a stream of dry air was passed through it, a large quantity of a chlorine compound. The ether was therefore prepared from silver fumarate and isobutyl iodide in the same way as the ethyl fumarate already described.

The action is not so violent as when ethyl iodide is employed. An evolution of gas seemed to take place, consisting probably of isobutylene, which would account for the small yield of ether obtained. From 40 grams of fumaric acid only 20 grams of the ether were obtained. Isobutyl fumarate is an oily liquid, which, under a pressure of 160 mm. boils at 170°; it was not, however, obtained pure. It contained some fumaric acid, from which it was found impossible to free it by redistillation.

The following analyses may be adduced, although on account of this impurity, the numbers agree only approximately with the calculated percentages:—

I. 0·1488 gram of the substance gave 0·1146 gram H_2O and 0·3369 gram CO_2.

II. 0·2178 gram gave 0·1683 gram H_2O and 0·4932 gram CO_2.

		Found.	
Calculated for $C_{12}H_{20}O_4$.		I.	II.
Carbon	63·16	61·75	61·76
Hydrogen.....	8·77	8·56	8·59
Oxygen.....	28·07	—	—
	100·00		

The action of sodium isobutylate on the isobutyl fumarate was conducted as follows:—Sodium isobutylate not being very soluble in isobutyl alcohol, in order to avoid too great dilution, less of the latter was added than was required for complete solution. The isobutyl fumarate was added to the partly dissolved sodium isobutylate in the proportion of one molecule of the former to two atoms of sodium. The mixture gradually dissolved to a reddish-brown liquid; the reaction, however, proceeded much more slowly than in the experiments already described. After standing some hours, the product was heated for an hour over the water-bath, and after addition of water saponified with excess of potassium hydrate solution. The aqueous solution having been separated from the isobutylic alcohol, was acidulated with nitric acid, a small precipitate of fumaric acid was filtered off, and from the filtrate, neutralised with ammonia, a lead salt was precipitated by means of lead nitrate. The acid, obtained by decomposition of the lead salt with sulphuretted hydrogen, formed a thick syrup, solidifying *in vacuo* to a deliquescent crystalline mass, which, however, after repeated crystallisation from aqueous and ethereal solution remained

still deeply coloured. On account of its small quantity, it was impossible to obtain the acid in a state pure enough for analysis. The analyses of the calcium and silver salts, however, given below, show that it has the composition of an isobutyl malic acid corresponding to the formula, $\begin{matrix} CH(OC_4H_9)COOH \\ | \\ CH_2.COOH \end{matrix}$.

By neutralising the aqueous solution of the acid with calcium hydrate solution and boiling, an insoluble crystalline calcium salt was obtained, which, when dried *in vacuo*, gave on analysis the following results:—

I. 0·1886 gram of the substance gave 0·0919 gram H_2O, 0·2775 gram CO_2; in the residue 0·0582 gram CaO and $CaCO_3$, which gave 0·1116 gram $CaSO_4$, giving by calculation 0·0122 gram CO_2 and 0·03282 gram Ca.

II. 0·1609 gram gave 0·0774 gram H_2O, 0·2331 gram CO_2; in the residue 0·0522 gram CaO and $CaCO_3$, which gave 0·0949 gram $CaSO_4$, giving by calculation 0·0131 gram CO_2 and 0·02791 gram Ca.

		Found.	
Calculated for $C_8H_{12}CaO_5$.		I.	II.
Carbon	42·11	41·89	41·73
Hydrogen	5·26	5·41	5·34
Calcium.....	17·54	17·40	17·35
Oxygen	35·09	—	—
	100·00		

The silver salt was obtained as an insoluble flocculent precipitate by adding silver nitrate to the aqueous solution of the acid, neutralised with ammonia. On analysis the carbon was found $\frac{7}{10}$ per cent. too low, and the silver correspondingly high, this discrepancy with the theoretical numbers being probably due to the presence of fumaric acid.

To get rid of this impurity, a solution of the soluble barium salt was prepared by neutralising an aqueous solution of the acid with barium hydrate, the barium fumarate which separated out on evaporation was filtered off, and from the filtrate the silver salt was obtained by fractionated precipitation with silver nitrate. The analysis of the last precipitated fraction gave the following results:—

I. 0·2022 gram of the substance gave 0·0525 gram H_2O, 0·1738 gram CO_2, and 0·1083 gram Ag.

II. 0·2555 gram gave 0·0659 gram H_2O, 0·2185 gram CO_2, and 0·1371 gram Ag.

		Found.	
Calculated for $C_8H_{12}Ag_2O_5$.		I.	II.
Carbon	23·76	23·44	23·32
Hydrogen.....	2·97	2·88	2·87
Silver	53·47	53·56	53·66
Oxygen.....	19·80	—	—
	100·00		

The formation of these acid ethers by the action of sodium alcoholates on fumaric ethers is analogous to that of malic acid from fumaric acid (*Annalen*, **192**, 80) effected by F. Loyde, by heating the latter with sodium hydrate solution. While, however, for the latter reaction heating for 100 hours is required, ethyl fumarate reacts with sodium ethylate at the ordinary temperature with evolution of heat. The ease with which the reaction takes place is no doubt partly due to the fact that the ether is a liquid. Sodium fumarate when heated over the water-bath with alcoholic sodium ethylate, yields no ethyl malic acid.

An attempt to isolate the sodium compound did not succeed; the formation, however, of a sodium ethyl malic acid as an intermediate product is very probable.

An experiment, in which chloracetic ether was added to the product of the reaction of alcoholic sodium ethylate on ethyl fumarate, showed that the reaction took place in the same sense as when an alcohol iodide was added.

When sodium ethylate, free of alcohol, is added to ethyl fumarate, an addition-product is apparently formed, from which, by addition of alcohol iodide, the synthesis of homologous acids might possibly be effected. The presence of alcohol seems to be the cause of the replacement of the atom of sodium by hydrogen. The course of the reaction in the experiments described is to be represented no doubt by the following equations:—

$$CO_2C_nH_{2n+1}.CH : CH.CO_2.C_nH_{2n+1} + NaO.C_nH_{2n+1} = CO_2C_nH_{2n+1}.CH(C_nH_{2n+1}).CHNa.CO_2C_nH_{2n+1}.$$

$$CO_2C_nH_{2n+1}.CH(OC_nH_{2n+1}).CHNa.CO_2C_nH_{2n+1} + HOC_nH_{2n+1} = CO_2C_nH_{2n+1}.CH(OC_nH_{2n+1})CH_2.CO_2C_nH_{2n+1} + NaOC_nH_{2n+1}.$$

The research will be prosecuted in the direction indicated above, and the corresponding reactions with maleic acid will be included within the scope of the investigation.

In conclusion the writer begs to express his indebtedness to Professor Wislicenus for advice and help received during the progress of this research.

L.—*On Ammonium Nitrite, and the Reaction between Hydrogen and Nitric Oxide in presence of Spongy Platinum.*

By Lewis T. Wright.

In a former paper (*Chem. Soc. J.*, 1879), when remarking on the action of heat upon solutions of ammonium nitrite, I stated that when a certain degree of concentration is reached, continued boiling causes a considerable loss, and that a portion of the salt thus lost appears in the distillate. It was then my intention to investigate quantitatively the decomposition of this interesting ammonium salt, but I have not yet gone sufficiently far with the inquiry to be able to give a full account of the decomposition. I will, however, describe an experiment which satisfied me that ammonia, ammonium nitrite, and nitric oxide are certainly present amongst the products of the decomposition.

A 300 c.c. glass flask was fitted up with a vulcanite stopper pierced with three holes, one for a safety tube which was immersed in water to a depth sufficient to produce seal, one for an ordinary tap-funnel, and the third for a tube leading to an upright spiral condenser, around which cold water was circulated. To the outlet of the condenser was attached a small bottle, with a connection for leading the gaseous products to a three-way piece which was connected with a hydrogen generating apparatus, also with a cylinder, 12 inches by 2½ inches, charged with freshly slaked lime. On the outlet of this cylinder was a nitrogen-bulb charged with acidulated ferrous sulphate. A solution of ammonium chloride was let into the generating flask and boiled in a current of hydrogen. When it was judged that all air had been expelled from the apparatus, and the solution of ammonium chloride had cooled, a little potassium nitrite solution was run into the flask, the hydrogen shut off, and heating recommenced. The bulbs containing the acid ferrous solution were frequently recharged, and always showed nitric oxide reaction; when about 100 c.c. had distilled over into the small bottle, hydrogen was blown through, and the distillate examined. Whether the potassium nitrite solution had been alkaline, acid, or neutral, large quantities of free ammonia were present in all experiments with a considerable quantity of ammonium nitrite. It was evident that the reaction was more complicated than is expressed by the ordinary equation—

$$NH_4Cl + KNO_2 = N_2 + KCl + 2H_2O.$$

I hope soon to be able to publish some quantitative evidence bearing on this subject.

Recently G. S. Johnson (*Chem. Soc. J.*, March, 1881) has used ammonium chloride and potassium nitrite for generating nitrogen in his experiments on the synthesis of ammonia from that body and hydrogen in presence of spongy platinum. As the synthesis of ammonia under such circumstances appears to me to be a matter of very considerable interest, I have made some experiments with the object of confirming his experiments or otherwise. My apparatus differed somewhat from his, as did the final result.

The apparatus first used consisted of a 300 c.c. evolution flask containing strong solution of NH_4Cl and KNO_2 fitted with safety-tube and connection to an upright cylinder closely packed with freshly slaked lime. A connection from a hydrogen-generating apparatus also led into the inlet of this cylinder; on the outlet were attached in succession six long tubes closely packed with glass beads and charged with freshly prepared concentrated acid ferrous sulphate. These tubes form the best gas-washing apparatus I am acquainted with, and being placed horizontally in a suitable stand, admit of easy revolution, and consequent renewal of washing surface. These six tubes were thought to be fully equal to the eight different pieces used by Johnson for the absorption of NO. On the outlet of these tubes was placed a small glass flask containing Nessler solution, through which the gases passed on their way to the spongy platinum which filled a tube 12 inches long, $\frac{1}{4}$ inch diameter. A nitrogen bulb charged with Nessler solution completed the apparatus.

When hydrogen and nitrogen in the proportion of three to one (as nearly as possible) were passed through, it was found impossible to avoid the formation of ammonia in the spongy platinum tube; and when weak sulphuric acid solution was placed in the nitrogen bulb in place of Nessler solution, amounts of ammonia equal to 3 or 4 mgrms. were easily found by neutralisation. So far no means had been taken to ascertain whether the mixed gases entering the platinum tube were free from nitric oxide, but on breaking joint at this point, the issuing gases were found to smell of what I judged to be nitrous acid. Freshly prepared test-papers (iodide of potassium and starch-paste) placed directly in the current of the gases showed no reaction, but similar papers in a beaker inverted over the issuing gases so as to admit of mixture with air, were soon discoloured. The beaker smelt strongly of nitrous acid. Repeated experiments always gave the same results, viz., production of ammonia and evidence of nitric oxide. Between every two experiments, I burnt out the ammonia from the platinum in a current of air. It was not until large quantities of the gases had passed through the tubes containing ferrous sulphate that the ferrous solution developed a faint brown-yellow colour. It was only too evident that they had failed in arresting all the nitric oxide.

Before dismantling the apparatus, I studied the effect of hydrogen and spongy platinum upon nitrogen obtained from NH_4Cl and KBrO. The apparatus was recharged with fresh reagents, a strong solution of potassium hypobromite being first placed in the evolution flask and ammonium chloride run in through the tap funnel. Nitrogen obtained by this means did not develop ammonia when mixed with an excess of hydrogen in the presence of spongy platinum either in the heat or in the cold, but a minute trace of a solid acid body collected as a white sublimate inside the tube, and being driven over by heat into pure water, was obtained in quantity requiring 0·5 mgrm. ammonia for neutralisation. This acid was due no doubt to some impurity present in the nitrogen.

In the place of hypobromite and ammonium chloride evolving nitrogen, I used dry ammonium nitrate for the purpose of evolving nitrous oxide, which is known to be more or less contaminated with nitric oxide when procured from that salt. The flask containing the ammonium nitrate was heated gently on a sand-bath, the nitrous oxide being occasionally tested and found to contain small amounts of nitric oxide. In these experiments traces of ammonia were formed when the nitrous oxide and hydrogen were passed through spongy platinum. Nitric oxide was found on the inlet of the platinum tube, the ferrous sulphate again being inactive. The ammonia was produced in the cold, but the amounts were small in comparison with those found when nitrogen from ammonium chloride and potassium nitrate had been used. Sometimes the small quantity produced, 0·01 mgrm. in 30 minutes, did not reach the nitrogen bulb until the platinum was warmed. I tried the effect of heating the platinum whilst the mixed gases were passing through, but as was expected, the mixture fired, and frequent explosions took place, but even then I did not notice any increased quantity of ammonia. From these experiments and some afterwards to be described, I infer that hydrogen does not react on nitrous oxide in the presence of spongy platinum to produce ammonia, the nitric oxide present being sufficient to account for the ammonia formed. Some additions were then made to the apparatus in the shape of two large bottles filled with pumice, and two more long tubes, with beads all charged with ferrous sulphate solution as before. The rest of the apparatus was emptied, washed out with distilled water, and recharged. It now had eight tubes and two bottles for ferrous sulphate.

Experiments commenced *de novo* with nitrogen obtained from ammonium chloride and potassium nitrite, gave me no better results than before, the gases being imperfectly purified from nitric oxide, and amounts of ammonia equal to 3 or 4 mgrms. per hour being obtained as when the smaller apparatus had been used. I then felt convinced

that no ordinary amount of washing with ferrous sulphate would remove the last trace of nitric oxide.

R. Warington (*Chem. Soc. J.*, July, 1880) states of ferrous salts as an absorbent for nitric oxide, that "the method would probably fail to remove a small quantity of nitric oxide from a large volume of other gases in which the tension of nitric oxide was but feeble." J. Gay (*Compt. rend.*, **89**, 412) in his experiments with the different compounds formed by ferrous sulphate and nitric oxide, was able to recover the ferrous salt unaltered by driving out the nitric oxide with a current of hydrogen. He does not state, however, at what temperatures he experimented, but I have found that hydrogen will remove nitric oxide from its solution in ferrous sulphate at 16° to 18° C. even when the nitric oxide is present in but small quantities. I think there can be little doubt that ferrous sulphate is altogether unsuited for the purification of gases containing traces of nitric oxide, the compounds formed being of a very feeble character, reminding me somewhat of the water of crystallisation in sodium sulphate.

I now commenced some experiments with the object of investigating the action of hydrogen on nitrous and nitric oxides in the presence of spongy platinum. It is well known that nitric oxide and excess of hydrogen produce ammonia when passed over finely divided heated platinum. Ville (*Compt. rend.*, **41**, 938—987) has devised a method of analysis for nitrates based on this reaction, but he does not seem to be aware that the reaction takes place in the cold; he directs a temperature to be used *voisine du rouge.*

Experiments with Nitric Oxide and Hydrogen.

The apparatus consisted of an evolution flask containing a solution of ferrous sulphate in hydrochloric acid heated on a sand-bath and fitted with a tap-funnel charged with potassium nitrate solution; a tube from this flask was connected with a three-way piece which served to admit hydrogen; this led to a cylinder filled with freshly slaked lime, three tubes filled with beads and charged with pure sulphuric acid, then a small flask containing Nessler solution, a glass tube filled with spongy platinum, and a nitrogen-bulb for Nessler solution or standard sulphuric acid solution. With this apparatus, when the proportion of hydrogen to nitrogen was judged to be as 7 to 1, I did not notice the formation of any ammonia in the cold. It seemed as though the reaction would not take place; but on moderating the heat applied to the flask generating nitric oxide, so that the solution no longer boiled, and the hydrogen was only contaminated, so to speak, with nitric oxide, ammonia was easily formed in the platinum at the rate of about 3 mgrms. in five minutes even in the cold. I satisfied

myself by many experiments that ammonia was formed in the cold when the hydrogen was in large excess. A similar behaviour takes place at higher temperatures. Bloxam (*Chemistry, Inorganic and Organic*, London, 1867, 132) says "If two volumes of nitric oxide be mixed with five volumes of hydrogen and the gas passed through a tube having a bulb filled with platinised asbestos, the mixture issuing from the orifice of the tube will produce red vapours by contact with the air, which will strongly redden blue litmus, but if the platinised asbestos be heated with a spirit lamp, the hydrogen encouraged by the action of the platinum will decompose the nitric oxide, restoring the blue colour to the litmus." It will be seen by my experiments that if the hydrogen be present in large excess, the same reaction will take place in the cold.

Experiments with Nitrous Oxide and Hydrogen.

The behaviour of nitrous oxide was studied with the same apparatus, dry ammonium nitrate being substituted for iron mixture in the evolution flask. I was not successful in avoiding altogether the contamination of nitrous oxide with nitric oxide, but after very careful heating of the ammonium nitrate the nitrous oxide was much freer from the nitric oxide than I had expected. No efforts were made to purify the nitrous oxide from nitric oxide, for I was not then acquainted with any reagent suitable for the purpose. It was found impossible to avoid the formation of traces of ammonia in the platinum, but the amount in some experiments lasting one hour did not exceed 0·005 mgrm. The feeble quantities produced with varying proportions of hydrogen and nitrous oxide convinced me that they do not react to form ammonia in presence of spongy platinum. Experiments were tried in which the platinum was heated, but the explosions were so troublesome that I discontinued them. However, the heating did not cause any increased amount of ammonia to form.

Experiments to prove that Ammonia is not synthetically produced by the combination of Hydrogen and Nitrogen in presence of Spongy Platinum.

It is known that alkaline sulphites convert nitric oxide into nitrous oxide. Acting upon this information, I substituted sodium sulphite solution, to which had been added some potash, for acid ferrous sulphate solution, as absorbent for nitric oxide. I would have tried potassium pyrogallate, but from an experiment by Lechartier (*Compt. rend.*, **89**, 308), I thought that the action might not be complete. He shook up 53 c.c. of nitric oxide with potassium pyrogallate several times, and left them in contact for 12 hours, and after removing the pyrogallate he absorbed a further 3 c.c. with ferrous sulphate solution.

I fitted up a train of apparatus, consisting of evolution flask for nitrogen, from ammonium chloride and potassium nitrite, hydrogen-generating apparatus, cylinder charged with lime, two bottles charged with pumice saturated with alkaline sodium sulphite, eight long tubes as before used, one tube of large dimensions, 14 inches by 3 inches, filled with pumice, all saturated with alkaline sulphite, two long tubes with pure sulphuric acid, small flask for Nessler solution, tube filled with spongy platinum, and lastly, a nitrogen-bulb with Nessler solution. This cumbersome apparatus threw 5 inches water pressure when in full action. Two experiments of an hour's duration gave the following results:—

1st experiment	.....	·003 mgrm. NH_3
2nd „	.....	nil.

The platinum tube was heated with a Bunsen burner from time to time. The feeble trace of ammonia in the first experiment was, I have no doubt, due to a trace from a previous experiment.

I should mention that between all experiments with the spongy platinum I burnt out the ammonia in a current of air.

The conclusions I draw from the above experiments are:—

That nitric oxide is not completely absorbed by ferrous sulphate at ordinary temperatures.

That hydrogen reacts upon nitric oxide to produce ammonia in presence of cold spongy platinum when the hydrogen is in sufficient excess.

That nitrous oxide is not so acted on.

That nitrogen and hydrogen do not combine synthetically to produce ammonia in presence of spongy platinum—at least when the nitrogen is procured from ammonium nitrite, or ammonium chloride and potassium hypobromite.

LI.—*On the Colour Properties and Colour Relations of the Metals of the Iron-Copper Group.*

By Thomas Bayley.

A dilute solution of nickel sulphate is green, and can be exactly simulated by a mixture of iron and copper. When 7 parts of iron and 20 parts of copper are dissolved, as sulphates, in excess of a mixture of dilute sulphuric and nitric acids, a bluish-green solution is obtained, which is complementary to solutions of cobalt, and produces on admix-

ture, at 18° C., with 6 parts of the latter metal dissolved as sulphate, a solution devoid of colour, but partially opaque.

This bluish-green mixture of copper and iron, compared with a solution of nickel sulphate, appears of a bluer tint, and a mixture of the sulphates of iron and copper, in order to simulate nickel sulphate, must contain a greater proportion of iron. The exact quantities required depend upon the temperature of the solution and upon the state of concentration. At 5°, in order to produce the tint of nickel solutions, about 1 part of copper and $1\frac{1}{2}$ parts of iron are required, if the solutions are dilute; but if this mixture be raised to 15°, and compared with dilute nickel sulphate at the same temperature, it is found to have become decidedly yellower, and now a mixture of equal parts of iron and copper is similar to the nickel solution.

But direct comparison of iron and copper mixtures with nickel solutions in this manner is inadequate to determine with the greatest accuracy the quantitative colour relations of the three metals, and I have therefore resorted to the method which has been already used successfully to determine the quantitative colour relations of iron, copper, and cobalt. For this purpose solutions were prepared as before, containing respectively 5 grams of each metal as sulphate. The solution of nickel was prepared by dissolving 13·163 grams of the sulphate, rendered anhydrous by ignition to low redness, in a considerable quantity of water, adding sulphuric acid and diluting to a litre.

A solution containing 20 parts of copper, 7 of iron, and 6 of cobalt, and chromatically neutral at a temperature of about 18°, being taken as the standard, the copper and nickel solutions were mixed in white glass cylinders, with 6 parts of cobalt at the same temperature, until after repeated trials a colourless mixture was obtained. This contained copper 13 parts, nickel 8·75 parts, and cobalt 6 parts, and was undistinguishable from the standard mixture. There are thus two colourless solutions containing the same quantity of cobalt, neutralised in the one case by 20 parts of copper and 7 of iron, and in the other by 13 parts of copper and 8·75 parts of nickel. As a consequence of this, 8·75 parts of nickel are equal, at any rate as regards quality of colour, to 7 parts of iron and 7 of copper. Considering only the three metals copper, nickel, and cobalt, their colour-equivalents are 13, 8·75, and 6 respectively, and their colour coefficients are (Cu) 1, (Ni) 1·48, (Co) 2·16. The colour coefficients of copper, iron, and cobalt, regarded as a neutral colour group, are (Cu) 1, (Fe) 2·85, (Co) 3·33; and since the quantities of cobalt involved in the two cases were identical, it is necessary to multiply the former series of coefficients by 1·54 to make the coefficients of cobalt equal in the two series, which are then capable of comparison—

Cu.	Ni.	Fe.	Co.
1	—	2·85	3·33
1·54	2·27	—	3·33

The coefficient thus obtained for nickel differs considerably from that suggested temporarily in my former paper (viz., 1·05), which was obtained from the consideration of earlier experiments made in Prof. Galloway's laboratory in Dublin (*Proc. R. I. A.*, 2 ser., **3**, Science), involving only nickel and cobalt, which do not in any proportions yield a colourless mixture, but it is interesting to observe how the relation between the sequence of the colour-equivalents and the manner in which the metals follow one another in affinity for oxygen and in electrochemical order still holds good. It is also worthy of notice that the coefficient of copper in the second series is increased by 0·54, while the coefficient of nickel is lower than the coefficient of iron by the same amount, and the sums of the two series are equal. This rise in the colour coefficient of copper is apparent and not absolute, because, as is seen by the foregoing experiments, and by the study of its absorption spectrum, the nickel causes absorption in two regions, the red and the violet, the former being the region absorbed by copper, and the latter by iron solution.

In this respect nickel differs from copper, iron, and cobalt, which in the state of sulphate of the oxides, and unassociated with other bases, have only one region of absorption, at least in the visible spectrum. Nickel thus, by virtue of its double absorption, simultaneously enacts the part of both iron and copper, for at 15—20° 8·75 parts of nickel replace 7 parts of iron in a grey mixture, and also reinforce the copper present, so that 13 and not 20 parts are required.

It must not be forgotten that chromium, manganese, and copper, and even nickel itself, are capable, in aqueous solution, of existence in more than one colour state, and of causing absorption or transmission in more than one of the three regions of the spectrum previously defined. Besides the blue salts of cupric oxide (CuO) and the colourless salts of cuprous oxide (Cu_2O), there are also, as is known, coloured salts of the latter. If to the deep blue solution of copper sulphate in ammonia a slight excess of strong sulphurous acid be added, the blueness is destroyed, and the liquid becomes sometimes colourless, but more often yellow. This colourless or yellow solution changes frequently almost instantaneously, at other times more slowly, into a deep copper-red liquid. The copper-redness of the liquid is caused by transmission in the "red region," and the solution consequently resembles in colour the reflection from metallic copper. Indeed the resemblance is perfect, and very striking under certain circumstances.

The copper-red solutions of copper are complementary to the blue

solutions; on dilution they become brownish-yellow, and finally colourless; mixed with potash and boiled, they deposit yellow cuprous oxide. During the process for determining carbon in iron by combustion, when the metallic copper deposited during digestion of the sample with copper sulphate is being dissolved in acidulated copper chloride, the red salts of copper usually manifest themselves, the opacity and approximate blackness of the liquid being due to admixture of the red salts with the excess of greenish-blue chloride of copper.

The blue solution of nickel sulphate in ammonia treated with sulphurous acid until the acid sometimes turns greenish-yellow, but often becomes pure yellow, and the latter solutions examined by the spectroscope show absorption in the violet region only, thus resembling iron salts. If cobalt sulphate be substituted for the nickel salt, a magnificent bright orange-coloured solution results. The nickel and cobalt solutions thus obtained by the use of sulphurous acid, on dilution or on standing, again become green and pink respectively.

The power of nickel to replace copper and iron remains when the nature of the light is changed. The solution of iron, copper, cobalt, which is colourless and opaque in diffused daylight, is dark green in gaslight, but a solution colourless and opaque in gaslight can be prepared, and has the composition iron 5, copper 20, cobalt 12 (or thereabouts, because no doubt the nature of gaslight varies). In daylight this solution appears pink. These equivalents were determined by comparing trial mixtures with distilled water, the water and the mixtures being contained in white glass cylinders, held a few inches above a white surface illuminated by the gas. A similar result is obtained by replacing the 5 parts of iron and 5 parts of the copper by 6·25 parts of nickel, for a solution containing nickel 6·25, copper 15, cobalt 12, was colourless in gaslight.

The grey solutions—and by this name are designated the mixtures of copper 20, cobalt 6, iron 7, and copper 13, cobalt 6, nickel 8·75—have some properties in common and some points of difference. They are both colourless at 15—20°, and at this temperature their absorption spectra are identical. The iron solution at lower temperatures is violet, and at higher temperatures greenish-yellow. At 5° the solution is perceptibly violet, at 30° perceptibly green, and at the boiling point strongly green. The grey nickel solution, on the other hand, does not vary perceptibly between the ordinary temperature and the boiling point. The grey iron solution, on concentration or in great thickness, preserves its main characteristics, but the coefficient of iron apparently diminishes slightly. The grey solution containing nickel varies less than the grey iron solution, and is scarcely affected by concentration to a considerable extent.

The white light absorbed by the grey solutions and the residual

white light transmitted are not ordinary white light. By reference to the accompanying diagram of the absorption-spectra of these solutions, the nature of the light is seen. The transmitted portion is compound white light, consisting of the rays of two complementary regions of the spectrum. Of the two transmitted bands, one has its centre in the yellow, and the other in the indigo. The diagrams represent the spectra obtained with a dense flint-glass prism. The yellow band in moderate thickness of the grey liquid consists of yellow fringed by red and green. As the thickness of the absorbent increases, the band dwindles until it consists only of yellow. The centre of this band is situated in the yellow part of the spectrum between D and E, but very near the former. The other band has its centre in the indigo between F and G, but nearer to the latter than to the former;* as the depth of the grey solution increases, the bands gradually disappear. The centres of the complementary transmitted bands are the boundary lines of the three regions that characterise the transmission and absorption-spectra of the aqueous solution of the metals of the group under consideration. For as the quantity of iron increases, the boundary of the dark band in the violet continues to approach the centre near G, and in the same manner the dark band of copper approaches the limit near D. The cobalt band has its limits in both centres. Of course the absorption-bands of the metals when in solution have not these limits; the absorption-band of iron, for instance, extends beyond the limit even in the diagram.

The nature of the light transmitted by the grey solutions accounts for the properties of these liquids. If the opacity and greyness were owing to a gradual suppression of all the rays in the spectrum in the proportions constituting ordinary white light, the colours of objects would be altered only in intensity and not in quality when seen through the solutions. As it is, the colours are extinguished altogether or considerably altered, when they are due to rays in the violet, green, or red regions of absorption, and altered very little, or not at all, when due to rays in the intermediate regions of transmission. A red-hot platinum wire appears lemon-yellow, because the red rays it contains are absorbed, and the yellow rays transmitted. The radiation from red-hot platinum contains only a small portion of the waves of higher refrangibility, and there is consequently a predominance of yellow light.

* The positions of the two complementary lines in the spectrum as fixed by these experiments agree with the position assigned to them by Prof. Grassmann, who says (*Phil. Mag.*, 1854):—"The yellow lies between D and E of Fraunhofer, and about three times as far from E as from D, the indigo extends from the middle of the space between the lines F and G, almost to the line G, so that any indigo which lies between these limits furnishes white with any yellow which lies near the position already described.

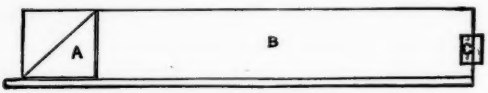
Since the grey solutions owe their chromatic neutrality to the combination of the two complementary transmitted beams, and since these combine in definite proportions to produce white light, it follows that unless the composition of daylight is invariable, the solutions cannot always be colourless. The light of the sun is essentially yellow, a cloud illuminated by the direct solar ray is yellow compared with the cloud on a clear but not bright day, and the sun itself is yellower than the illuminated cloud. Ordinary diffused daylight in the morning differs from diffused daylight in the evening, when the beams pass more obliquely through the atmosphere. As the intensity of solar illumination increases, of course the rays of all refrangibilities increase, but the rays in the region of the yellow transmitted beam appear to increase more rapidly than the rays in the indigo region. For this reason the colour of the grey solutions is not invariable, and the term must be understood to refer to solutions grey under certain meteorological conditions. The grey solutions of the composition and at the temperatures defined, are colourless in clear diffused daylight at midday; in the evening they have a tendency to violet, and in bright sunlight they look yellowish-green. The sun itself looks yellower through the grey solutions than when observed directly. On a foggy day the solutions are distinctly greenish, and the coloration increases with the density of the fog. Probably the observation of a standard white surface through a long column of grey solution might be used to indicate the variations in the nature of daylight.

The grey solutions, prepared by substituting the red salts of manganese for the cobalt salts, have the same general properties as the other grey solutions, and their absorption-spectra have the two bright bands in the yellow and in the indigo. Grey solutions containing chromium, when concentrated or observed in great thickness are often found to be imperfect, and in many cases the conditions appear to be the negative of those which exist in the case of the other grey solutions, the band in the yellow and, less frequently, the band in the indigo, being darker than the remaining parts of the spectrum. The colour properties of chromium are complicated and obscure, and are worthy of further and attentive study. It is, as I have shown, possible to prepare colourless chromic salts, by mixing the complementary green and red salts, but besides these there are colourless chromic salts which are formed spontaneously. I obtained a solution of this kind by allowing a red chromic solution to stand for some months. The red solution was prepared by adding strong ammonia in excess to chromic acid, and acidulating the resulting clear solution with nitric acid. At first it was indistinguishable from a moderately dilute cobalt solution placed side by side with it in the window, and was of a full pink colour. After a time it faded and began to exhibit a yellowish tint,

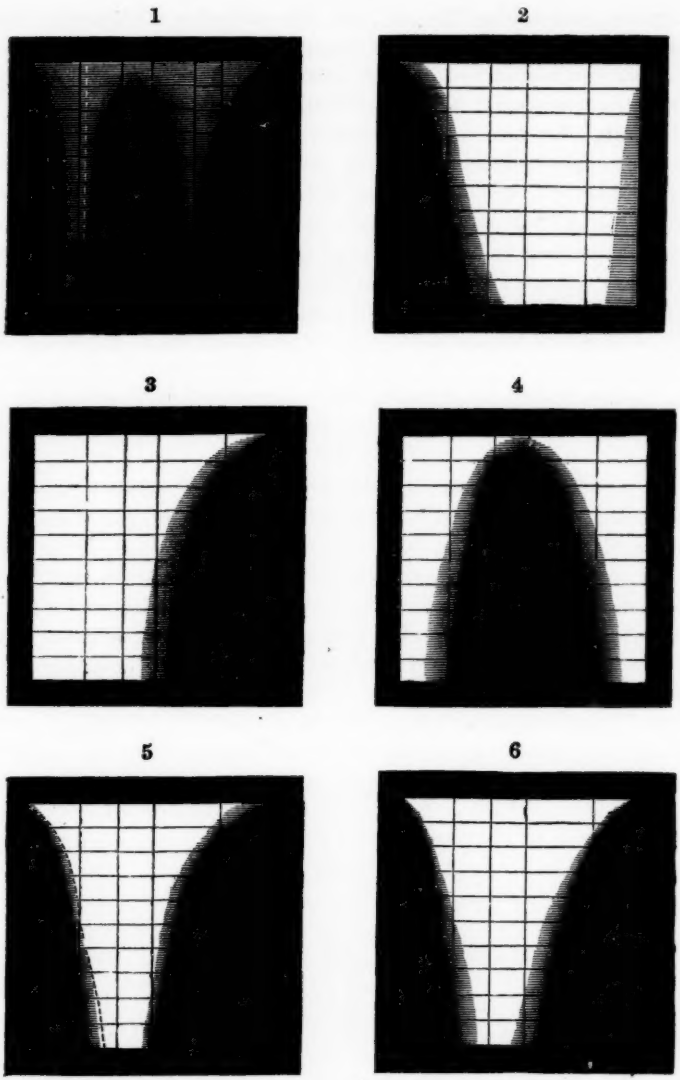
and ultimately became colourless. When the colourless liquid was evaporated to dryness, and the residue ignited and fused with alkaline carbonate and nitrate, yellow alkaline chromate was formed.

An illuminated surface is extinguished when viewed through a sufficient thickness of the grey solutions, the thickness required corresponding to the degree of illumination of the surface. I hope to make use of this fact to determine the illumination of metallic surfaces in an investigation of the conditions of reflection from copper, the results of which I hope soon to have the honour of laying before the Society. The photometric measurements obtained in this way would have the advantage of being absolute, and therefore independent of any external and arbitrary standards.

The diagrams illustrating this paper show the effect upon the spectrum of increasing thickness of the solutions; the method employed was essentially the same as that used by Gladstone. The apparatus consists of a wooden box about two feet long and four inches deep, the box is blackened inside and closed at each end by wooden plates. The plate at the anterior end is furnished with a fixed narrow slit on the median vertical line, and at the posterior end a rectangular hole is cut just large enough to allow the insertion of the prism C, which is made capable of rotation about its axis. In front of



the slit is the hollow prism A, this in section is a square decimeter, but it is divided into two chambers as shown. The chamber next to the slit contains the metallic solution, and the anterior chamber is filled with distilled water. This arrangement ensures the passage through the slit of light from any object situated in the direction of the longer axis of the instrument. The eye placed at C observes the spectrum, in which are visible the most conspicuous lines of Fraunhofer, and when the prism is filled and placed in position the appearance indicated by one or other of the diagrams, according to the nature of the solution, is observed. The solutions were made of equivalent chromatic strength, the copper solution contained 50 grams of metal per litre. The first diagram shows the spectrum of the grey liquid containing 50 grams of copper and equivalent quantities of iron and cobalt per litre. It also shows the spectrum of the grey nickel solution containing the same quantity of cobalt per litre as was contained in the grey iron solution. Diagram No. 2 shows the absorption-spectrum of copper, No. 3 the absorption-spectrum of iron, No. 4 of cobalt, Nos. 5 and 6 illustrate the absorption-spectra of a nickel solution, and of a



copper-iron solution of equivalent chromatic strength. By using solutions of known strength, and a prism of constant dimensions, it is possible to put on record more definite information than when solutions of unknown strength and a prism of indeterminate dimensions are used; and comparison with future experiments or with the work of other observers is made possible.

The black horizontal lines shown in the diagrams are obtained by

placing fine wire across the slit, at intervals of a centimeter; these horizontal lines and the lines of Fraunhofer subdivide the spectrum into rectangles, and so facilitate observation. These coloured solutions of equivalent chromatic strength do not appear equally coloured to the unaided eye, the iron solution seeming much less deeply coloured than the copper solution, and the copper solution than the cobalt solution, although each decomposes the same amount of white light.

This, I think, is because the rays absorbed by the iron solution, the violet rays, are less easily appreciated by the eye than the more easily appreciated red rays absorbed by copper, and the still more easily appreciated green rays absorbed by cobalt.

The experiments described in this paper point to the following conclusions:—

The colour effects of nickel in ordinary solutions can be produced by a mixture of copper and iron in varying and widely different circumstances.

A colourless opaque solution, resembling the colourless opaque iron-copper-cobalt solution, can be produced by mixing nickel, copper, and cobalt solutions.

These colourless opaque solutions in sufficient thickness transmit no light, and the light transmitted by solutions of less thickness is compound white light made up of the rays of two complementary beams, one having its centre in the yellow, and the other in the indigo of the spectrum.

Under certain circumstances, as described, nickel forms yellow solutions, and copper forms copper-red solutions, while under similar circumstances cobalt forms orange solutions.

LII.—*Action of Humic Acid on Atmospheric Nitrogen.*

By E. W. Prevost, Ph.D.

Of the various problems which present themselves to the agricultural chemist, perhaps not one is of greater interest than that of the supply of nitrogen to the soil. Many theories have been propounded to account for the supply, but not one of them will account for the whole supply. Amongst these, the humic acid theory is not the least remarkable. This states that the humic acid in the soil is capable of absorbing nitrogen directly from the air, and of transforming the nitrogen so absorbed into ammonia. Bretschneider (*Chem. Ackersm.*,

1871) found that the presence of humic acid greatly promotes the absorption of nitrogen from the air, and that the quantity absorbed depends on the amount of acid present. Déhérain (*Compt. rend.*, **73**) observed that humic acid mixed with a solution of potash also absorbed nitrogen to the amount of 7·2 per cent. Again, in the report of the *Landw. Versuchs.-Stat.*, **18**, 457, E. Simon gives the result of experiments made by him on the same subject. The experiments were as follow:—(1.) Humic acid and water sealed up in a flask for 14 days absorbed a part of the nitrogen also enclosed in the flask, and ammonia was produced in such quantities as could be easily detected. (2.) Nitrogen was passed for 12 hours through a Liebig's potash-bulb containing water and humic acid; the solution afterwards gave a precipitate with platinum tetrachloride. (3.) Humic acid and water in a glass flask, whose mouth was closed by a caoutchouc stopper which was occasionally opened, contained ammonia after 14 days.

The results obtained by Simon appeared so remarkable, that as I had not been able to gather any further information on this subject, I decided on repeating the experiments, so as to determine if possible the rate at which the absorption took place.

Two samples of humic acid were employed, the one (1) prepared by Messrs. Hopkins and Williams yielding 0·225 per cent. of ammonia when distilled with magnesia and a little potash, the other (2) prepared by myself from peat according to the method recommended by Detmer (*Landw. Versuchs.-Stat.*, **14**), and yielding 0·77 per cent. of ammonia. Both samples possessed the properties of humic acid as described by Detmer, with the exception that that prepared by myself from peat was of a slightly brownish tint instead of black.

Experiment (*a*).—Three grams of humic acid (2) were hermetically sealed up in a glass tube with 20 c.c. of water and 76·6 c.c. of air, and left exposed to the light for 18 months.

Experiment (*b*).—An excess of acid (1) was boiled with a solution of potassium carbonate, and the dark solution so obtained was found to contain 0·0000476 gram NH_3 per 1 c.c. 100 c.c. of this solution were placed in a large flask, and air purified from ammonia by passing through wash-bottles containing glass moistened with sulphuric acid and Nessler's solution was caused to bubble through the solution twice a day for three months, so that roughly speaking the solution was brought in contact with 300 litres of air = 237 litres N.

Experiment (*c*).—Humic acid (1) and water were, by means of the apparatus briefly described above, also brought in contact with 300 litres of air in a large glass flask.

Experiment (*d*).—Humic acid (2) and water were placed in a flask, into the neck of which was fitted by means of a cork a doubly bent

glass tube, which when partially filled with water could act as a pressure-gauge, indicating by change of level any diminution of pressure occurring inside the flask, due to absorption of the nitrogen of the enclosed air; the water also would shut off communication from the external air.

It was expected that these experiments would show, firstly, if there were any absorption (*d*); if there were absorption of the nitrogen, whether all the nitrogen of the air would be removed (*a*); whether the absorption occurred when the acid was in the free state (*c*); also when there was free acid in the presence of potassium humate (*b*). Experiments (*b*) and (*c*) would also determine the rate at which the absorption took place, if the solutions were periodically examined for ammonia.

The results of the experiments were as follows:—

Experiment (*a*).—When the tube was opened, it was found that a slight reduction of the volume of the air had taken place, as after making the proper allowances for barometric pressure, solution of the air in water, &c., there still remained 1·97 c.c. of air to be accounted for. The water, which was colourless, was proved to contain ammonia in quantity equivalent to 0·19 c.c. N; the remainder of the air had probably been employed in converting a portion of the ammonia into nitric acid, as nitric acid was present, and the amount was determined by the zinc-copper couple; but as the quantity (of a substance reducible by the couple) had not been estimated in the original substance at the commencement of the experiment, no calculations can be made from the analytical figures obtained.

The residue when dried yielded 0·172 per cent. of ammonia, and when treated with the zinc-copper couple it yielded ammonia equivalent to 0·251 per cent. of N_2O_5. The following figures show that certainly no appreciable quantity of ammonia was produced during the 18 months that the experiment lasted.

In 3 grams of original acid there were 0·527 c.c. of N as NH_3.

After contact of 3 grams with air and water, there was found in the water 0·19 c.c. N as NH_3, and in the residue 0·339 c.c. N as NH_3; total = 0·529 c.c. As some air was absorbed, it is possible that ammonia may have been formed and oxidised to nitric acid, but owing to the omission of the estimation of this acid at the commencement of the experiment, it is impossible to say how much of the above 0·251 per cent. of N_2O_5 was or was not originally present.

Experiment (*b*).—After exposure to 300 litres of air, the solution of potassium humate showed no increase whatever of ammonia. The analytical results show a slight diminution in the amount of ammonia present after the lapse of three months, as compared with the quantity present at the commencement of the experiment, but the

difference can only be due to experimental error, or else to the formation of a nitrate.

The figures are as follows:—

Ammonia in the original alkaline solution = 0·0000476 gram per 1 c.c.

Ditto, after three months, under circumstances mentioned above = 0·0000428 gram per 1 c.c.

Experiment (*c*).—No results were forthcoming, as owing to the severe frost in January the flask was broken and the liquid lost, but I might mention that there was apparently no change, as the water had remained up to January perfectly colourless.

Experiment (*d*) showed but little change of pressure taking place inside the flask, no more than would be expected when the fluctuations of the barometric pressure and temperature of the laboratory are taken into account; the water remained colourless, and no ammonia was obtained from the mixture except what was present in the original material.

Finding my results to be as described above, I exposed for several weeks in a room adjoining the laboratory, a solution of potassium humate containing humic acid, in excess, so that every opportunity was afforded for the absorption of nitrogen with production of ammonia, and for the absorption of free ammonia, but the solution when boiled with potash yielded only the faintest traces of ammonia.

The conclusions which I am bound to draw from these experiments are opposed to those of Simon and others. The cause of the difference is at present to me unaccountable, unless it be that the materials employed by us are not identical; still, as before said, the properties and the analysis agree with those described by Detmer, and also by Simon, with this exception, that whereas Simon's acid colours distilled water slowly, mine does not appear to dissolve at all in distilled water.

Experiment (*a*) may show an absorption of nitrogen and possible conversion into nitric acid, as Déhérain says; but as this absorption, if it takes place, does not appear to be very rapid, but in fact very slow, it cannot be considered as a very fruitful source of nitrogenous plant food. Perhaps if a very large column of nitrogen were left in contact with humic acid for a considerable time, some more satisfactory results might be obtained. This I had purposed doing, but circumstances have occurred which oblige me to postpone the experiment until some future date.

LIII.—*Experimental Researches on the Amalgamation of Silver Ores.*

By C. Rammelsberg.

The greater part of the silver imported into Europe is obtained, not from silver ores properly so called, but from argentiferous galena, the lead being either pattisonized or treated with zinc and then cupellated. A small quantity of silver is obtained from copper ores, and it is only at Kongsberg, in Norway, that native silver occurs in ores of sufficient richness to allow of the separation of the metal by smelting processes.

The richness of America in silver has long been proverbial, but at present, in consequence of political disturbances, the celebrated localities of Mexico and Peru contribute comparatively little to the entire production of the precious metal. On the other hand, the northern part of that continent has for the last quarter of a century become a fruitful source of silver. All the States and Territories on the west of the Missouri—Nevada, Utah, Colorado, Montana, Arizona, Idaho, Dacota, Oregon, and California, now produce the greatest amount of gold and silver, the value of which in 1877 was 90,000,000 dollars, near the half belonging to each of the two metals. It is important that the production of silver in the last seven years has increased from 1 to $2\frac{2}{3}$.

American silver ores are in general similar to the European, but the localities are more numerous and more extended. The Spanish miners, on their arrival in Mexico and Peru, being unable to employ the usual method of smelting for want of coal, a new process of treating silver ore, invented by Bartolomé de Medina in the sixteenth century, was soon applied in Mexico and in Peru. This is the amalgamation or the patio process (*el beneficio por patio*), a most remarkable process, which is still in use in the original manner, or modified, and must be considered as the chief mode of production of American silver.

The usual method of proceeding is well known. The ores, ground with water to a very thin slime, are mixed with common salt, magistral, and mercury, and the silver amalgam thereby formed is distilled.

The patio process is of high interest in a scientific point of view, and the reaction between the silver ores and the substances above mentioned has been made the object of chemical research. Karsten (*Der Amalgamations-process, Abhandl. d. Berliner Akad. d. Wissensch.* 1838 u. 1851) proved that magistral, prepared by roasting copper pyrites, contains as its active constituent sulphate of copper, which,

by aid of the common salt, is converted into chloride of copper. He pointed out the action of this chloride on silver, sulphide of silver, and silver ores, and assumed that the formation of amalgam on the reduction of silver depends partly upon the decomposition of the sulphide, whereby chloride of silver is formed, which is decomposed by the mercury, partly upon a direct action of the latter on the sulphide. Karsten has not given any numerical results; we do not know whether the decomposing reaction is perfect, and in general we cannot express by formulæ the exact reactions on which the patio process is founded.

I will now give the results of my own experiments concerning the chemical processes in American amalgamation, *i.e.*, the action of cupric chloride and cuprous chloride on silver, chloride of silver, sulphide of silver, sulphide of arsenic, and sulphide of antimony, and on complex combinations, particularly Rothgültigerz (sulpharsenite and sulphantimonite of silver).

I. *Cupric Chloride and Silver.*

With regard to this reaction, I have only to confirm the results obtained by Karsten. Silver is wholly changed into chloride, and cuprous chloride is formed—

$$2CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2.$$

Subchloride of silver, according to Fernandez, does not exist under these circumstances.

II. *Cupric Chloride and Silver Sulphide.*

According to Karsten the action is very slow and incomplete. Boussingault found that the decomposition takes place only in presence of sodium chloride. From 100 parts of Ag_2S he obtained 146 parts of insoluble matter containing silver, copper sulphide, and chlorine, but he did not analyse it. If we suppose the conversion of Ag_2S into AgCl to have been complete, the product would contain—

Silver	87·0	=	AgCl	115·8
Chlorine	28·8			
Copper	17·2	=	CuS	25·8
Sulphur	8·6			
Sulphur	4·4	=	S	4·4
				146·0

i.e., 6AgCl : 2CuS : S. Consequently the process would be—

$$3Ag_2S + 4CuCl_2 = 6AgCl + 2CuS + S.$$

In my experiments a determinate quantity of silver nitrate was precipitated by sulphuretted hydrogen, and the precipitate digested and boiled for a short time with a neutral solution of cupric chloride. The black deposit, after being washed and dried, was analysed.

100 parts of Ag_2S = Ag 87 and S 13, gave 152 parts of dry substance, containing—

Silver	86·5
Copper	22·5
Chlorine	28·4
Sulphur	13·0
	150·4

The substance contains all the silver and sulphide employed, and the analysis shows that 2Ag : Cu are present.

The decomposition of Ag_2S by $CuCl_2$ under these circumstances is therefore complete—

$$Ag_2S + CuCl_2 = 2AgCl + CuS,$$

and no cuprous chloride is formed.

	Calculated numbers.			
Silver	87·0	=	AgCl	115·6
Chlorine	28·6			
Copper	25·5	=	CuS	38·5
Sulphur	13·0			
	154·1			

No free sulphur is separated.

III. *Cuprous Chloride and Silver Sulphide.*

The chloride was precipitated by water from its solution in hydrochloric acid. The experiments were made in the same manner, but the solid cuprous chloride was easily changed by contact with atmospheric air into the green oxychloride, thereby causing some difficulties. An excess of the chloride was removed by washing the product with a solution of sodium chloride and a small quantity of hydrochloric acid. By these means part of the silver chloride is dissolved, and passes into the copper solution.

From 100 parts of Ag_2S I obtained 168 parts of dry substance having a black colour. Analysis, B with addition of the dissolved silver (AgCl)—

	A.	B.
Silver	79·4	87·0
Copper	50·1	50·1
Chlorine	26·1	28·6
Sulphur	12·4	12·4
	168·0	178·1

As Ag : Cu : S = 2 : 2 : 1, the action of cuprous chloride on sulphide of silver is—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cl_2S.$$

	Calculated for 100 p. c. of Ag_2S.			
Silver	87·0	=	AgCl	115·6
Chlorine	28·6			
Copper	51·1	=	Cu_2S	64·1
Sulphur	13·0			
	179·7			

With a concentrated solution of cuprous chloride in sodium chloride 100 grams Ag_2S yielded 164·4 of the black deposit, containing silver 78·3, copper 48·3, chlorine 25·8, sulphur 13·7. As 87·0 − 78·3 = Ag 8·7 had been dissolved by the sodium chloride in the form of 11·6 AgCl, the result of this trial confirms the former.

Boussingault asserts that the product of cuprous chloride and silver sulphide contains CuS. This would be possible if

$$2Ag_2S + Cu_2Cl_2 = 2AgCl + 2Ag2CuS,$$

i.e., 100 Ag_2S would yield 140 of solid products. We have seen that 180 are formed, and that silver in the metallic state is not present.

Still more erroneously is the process described by Malaguti and Durocher. According to them no silver chloride is to be found in the product, but only metallic silver—

$$Ag_2S + Cu_2Cl_2 = 2Ag + CuS + CuCl_2;$$

but it is impossible to believe that such a chemical process can take place. Did the French chemists not know that silver and cupric chloride cannot exist together?

By the common patio process, silver ores consisting of complex sulphides, and mixed with pyrites and blende, are but very imperfectly decomposed. Quite recently in Chile, Krölinke has invented a new method of treatment, consisting in the employment of cuprous chloride, prepared by heating a solution of cupric sulphate and common salt with metallic copper. The amalgamation is executed in closed

barrels, in a similar manner to that which was formerly adopted at Freiberg. To the contents of the barrels zinc and mercury are then added, and silver amalgam is formed in a few hours. The Krölinke process is said to give very good results.

I found that the product of treating silver sulphide with a solution of cuprous chloride in sodium chloride gives, when digested with zinc, a mixture of metallic silver and Cu_2S. On adding mercury silver amalgam is immediately formed.

IV. *Cupric Chloride and Arsenious Sulphide.*

The trisulphide, As_2S_3, artificially prepared and heated with a solution of the chloride, yielded 112 per cent. of a blackish-green deposit, containing S 37·60, Cu 65·74, As 2·16. On subtracting As and 1·38 S, as 3·54 As_2S_3 undecomposed, the remainder is CuS, and the reaction between the two substances is—

$$As_2S_3 + 3CuCl_2 = 3CuS + 2AsCl_3.$$

V. *Cupric Chloride and Antimonious Sulphide.*

The trisulphide, Sb_2S_3, precipitated by sulphuretted hydrogen and heated with a solution of the chloride, becomes black, and the residue after drying is a greenish-grey powder. The reaction would evidently be very simple,

$$Sb_2S_3 + 3CuCl_2 = 3CuS + 2SbCl_3,$$

were it not that the chloride is decomposed by water, and oxychloride, SbOCl, separated, so that the deposit contains not only a large proportion of antimony, but also chlorine and oxygen. From 100 per cent. Sb_2S_3 were obtained—

Copper	13·1	or	CuS	19·6
Antimony	49·1	,,	Sb_2S_3	36·0
Sulphur	16·7	,,	Sb	23·3
Chlorine, Oxygen	11·3	,,	Cl,O	11·3
				90·2

	Calculated $2CuS.Sb_2S_3.2SbOCl$.			
Copper	13·1	=	CuS	19·7
Antimony	49·0	=	Sb_2S_3	34·4
Sulphur	16·4	=	SbOCl	35·0
Chlorine	7·3		—	—
Oxygen	3·3		—	—
				89·1

It appears then that of 71·7 Sb contained in 100 Sb_2S_3, 49·1 are found in the solid product, and therefore 22·6 must be in the cupric solution; and of 28·3 S, 11 C must be looked for in that liquid. The presence of sulphuric acid is indicated by reagents, and a violet precipitate of oxychloride is observed to form on standing.

The composition of the deposit shows at once that it contains the elements of cuprous chloride, 2Cu : 2Cl; and hence the oxidation of the sulphur becomes intelligible. On the other hand it is difficult to explain why the third part of the antimonious sulphide has not been decomposed by the excess of cupric chloride. Perhaps a definite combination of CuS and Sb_2S_3 is formed.

VI. *Cuprous Chloride and Antimonious Sulphide.*

Sb_2S_3, after boiling with a solution of the chloride in sodium chloride, is converted into a black powder, the quantity of which is 118—120 per cent. of the sulphide. An analysis gave Cu 40·2, S 16·6, Sb 52·5; the other elements, chlorine and oxygen, were not determined. Hence it follows that 71·7 − 52·5 = 19·2 of Sb, and 28·3 − 16·6 = 11·7 of S were dissolved. The insoluble matter may be regarded as—

$$4Cu_2S.Sb_2S_3.4SbOCl,$$

Supposing the quantity of this product to have been equal to 124 per cent., its composition would be—

Copper	38·0
Sulphur	16·8
Antimony	53·9
Chlorine	10·6
Oxygen	4·7
	124·0

agreeing tolerably well with the numbers found by analysis.

It seems then that $\frac{1}{4}$th of the antimony and $\frac{5}{12}$ths of the sulphur, were dissolved by the aid of free chlorine. The liquid on standing deposits white antimonic acid.

VII. *Cupric Chloride and Light-red Silver Ore.*

To the most important and frequent silver ores belong the light-red silver ore (lichter Rothgültigerz, or Arsensilberblende), and dark-red silver ore (dunkler Rothgültigerz, or Antimonsilberblende). Some qualitative experiments by Karsten do not explain the action of the chlorides of copper on these minerals.

I have employed fragments of the former from Freiberg, in a pure state. The mineral, as is well known, consists of—

$$Ag_3AsS_3 = Ag65{\cdot}5,\ As15{\cdot}1,\ S19{\cdot}4.$$

100 grams of it, after being heated and boiled for a short time with a solution of $CuCl_2$, yielded a black insoluble substance amounting in two trials to 115 and 112 per cent. These experiments showed that the whole of the sulphur is contained in that part. Of the silver a small quantity (3 per cent.) was dissolved as chloride. Calculating on 65·5 silver (chlorine was not determined directly) the results were:—

	I.	II.
Silver	65·5	65·5
Chlorine	12·9	12·8
Copper	8·3	6·5
Arsenic	7·7	9·1
Sulphur	20·1	18·0
	114·5	111·9

Hence its follows that half of the arsenic was dissolved. These facts accord with the supposition that—

$$Ag_3AsS_3 : 3CuCl_2, \text{ or}$$
$$4Ag_3AsS_3 : 12CuCl_2 = 8AgCl, 2Ag_2S, 2CuS, As_2S_3, 5S,$$

whilst $2AsCl_3$ and $3Cu_2Cl_2$ are the soluble products. Assuming such an action, 100 parts of the ore should produce 113 parts of residue, containing—

Silver	65·5	or AgCl	57·0
Chlorine	14·3	„ Ag_2S	25·0
Copper	6·4	„ CuS	9·6
Arsenic	7·6	„ As_2S_3	12·4
Sulphur	19·1	„ S	8·2
	113·2		

It cannot be decided whether the residue contains Cu_2S and 6 atoms of free sulphur. Perhaps a new sulpho-salt is formed, consisting of—

$$(2Ag_2S, Cu_2S) + As_2S_3,$$

the mineral would then be decomposed by loss of one-third of the silver being replaced by an equivalent quantity of copper. For the amalgamation it would be desirable that all the silver should be converted into chloride, and all the arsenic dissolved, *i.e.*—

$$Ag_3AsS_3 + 3CuCl_2 = 3AgCl, 3CuS.$$

VIII. *Cupric Chloride and Dark-red Silver Ore.*

This mineral, $= Ag_3SbS_3$, contains Ag 59·8, Sb 22·5, S 17·7. In two experiments 100 parts of the ore yielded 129 and 127 parts of a greyish residue, containing—

	I.	II.
Silver	59·8	59·8
Copper	14·5	12·0
Antimony	22·1	22·3
Sulphur	17·2	16·3

Chlorine not determined.

Besides chlorine and copper, all the constituents of the ore are to be found in the product. Part of the silver is combined with sulphur, for, taking analysis I for calculation, we have a loss of 16·8 chlorine, and

Chlorine	16·8	=	AgCl	67·9
Silver	51·1			
Silver	8·7	=	Ag_2S	10·0
Sulphur	1·3			
Copper	12·0	=	CuS	18·0
Sulphur	6·0			
Antimony	22·3	=	Sb_2S_3	31·2
Sulphur	8·9			

the amount of S = 16·2.

Hence it appears that the action of cupric chloride on the ore would be—

$5Ag_3SbS_3 : 6CuCl_2$, or
$10Ag_3SbS_3 : 12CuCl_2 = 24AgCl, 3Ag_2S ; 12CuS ; 5Sb_2S_3$.

On this supposition 100 parts of the ores yield 129·7 parts of the products, containing—

Silver	59·8	=	AgCl	63·2
Copper	14·0	=	Ag_2S	14·1
Antimony	22·5	=	CuS	21·0
Sulphur	17·7	=	Sb_2S_3	31·5
Chlorine	15·7		—	—
	129·7			

As the chlorine was not determined, it is easy to see how the calculated proportions of AgCl and Ag_2S may differ.

IX. *Cuprous Chloride and Light-red Silver Ore.*

The chloride was dissolved in sodium chloride, the product being a grey powder. 100 parts of the ore yielded 124 parts of this substance, containing—

Silver	65·2*
Copper	23·8
Arsenic	9·2
Sulphur	19·4
Chlorine	6·4
	124·0

This experiment proves that the silver and the sulphur are wholly contained in the solid products; of the arsenic, however (15·1 parts in the ore), only three-fifths are present.

Supposing the process to be as follows—

$$3Ag_3AsS_3 : 5Cu_2CO_2 = Ag_9Cu_6As_2S_9Cl_2 \text{ and } 4CuCl_2,$$

we should have—

Silver	65·5	=	Ag	51·0
Copper	25·7	=	AgCl	19·3
Arsenic	10·1	=	CuS	38·6
Sulphur	19·4	=	As_2S_3	16·6
Chlorine	4·8		—	—
	125·5			

Hence it follows that the substance consists of—

$$7Ag, 2AgCl, 6CuS, As_2S_3.$$

When this substance is digested with ammonia, no trace of silver chloride is dissolved, because the latter, in presence of ammonia, decomposes the sulphide of copper, as will be seen further on.

X. *Cuprous Chloride and Dark-red Silver ore.*

Proceeding in the same manner I obtained 111 parts of a black product from 100 of the ore. The amount of silver was only 51 parts instead of 59·8, because 8·8 Ag was dissolved in the form of chloride. On adding this part, analysis would have given—

* Including 47Ag separated from the liquid.

Silver	59·8
Copper	13·1
Antimony	22·5
Sulphur	18·3

Hence it appears that the action is—

$$2Ag_3SbS_3 + Cu_2Cl_2 = Ag_6Cu_2Sb_2S_6Cl_2,$$

which may be considered as—

$$2Ag,2AgCl,Ag_2S,2CuS,Sb_2S_3, \text{ or as}$$
$$2AgCl,2Ag_2S,Cu_2S,Sb_2S_3,$$

and 100 parts of the ore should then give—

Silver	59·8
Copper	11·7
Antimony*	22·5
Sulphur	17·7
Chlorine	6·6
	118·3

XI. *Silver Chloride and Cuprous Sulphide in presence of Ammonia.*

From the preceding experiments it appears that silver sulphide and copper chloride are changed into silver chloride and copper sulphide. According to Karsten on treating them with ammonia, silver is reduced to metal, while chloride of copper is dissolved in ammonia. We should then have—

$$2AgCl + Cu_2S = 2Ag.CuS.CuCl_2.$$

On the contrary, Malaguti and Durocher assert that silver and sulphide of silver are formed, *i.e.*—

$$4AgCl + Cu_2S = 2Ag + Ag_2S + 2CuCl_2.$$

My own researches were extended to both the sulphides of copper, Cu_2S and CuS.

1. *Behaviour of* Cu_2S.—A determined quantity of nitrate was precipitated as AgCl, and heated with a weighed quantity of Cu_2S and ammonia.

a. 2 mols. Ag_2S and 1 of Cu_2S were taken. From $2Ag_2S = 287$ I obtained 286·1 of grey crystalline matter, containing silver 195, Cu 56·7, S 29·2, *i.e.*, Ag_2CuS. It is easy to prove that this substance contains metallic silver, and is consequently 2Ag.CuS. The deficient

* Including 47Ag separated from the liquid.

Ag (216−195 = 21 parts) would be separated from the blue liquid by hydrochloric acid.

b. When 4 mols. AgCl = 574 and Cu_2S were employed, 395 parts of a grey product remained, containing only a trace of copper, and consisting essentially of $2Ag,Ag_2S$.

The assertions of Karsten and Malaguti are correct, the effect depending upon the proportion of the two bodies.

2. *Behaviour of* CuS.—The sulphide was precipitated by sulphuretted hydrogen, and the proportion was 4AgCl : CuS. After digestion with ammonia a black residue was obtained, consisting of $2AgCl.Ag_2S$:—

$$4AgCl + CuS = 2AgCl,Ag_2S + CuCl_2.$$

I have not repeated the experiment with half the quantity of the chloride; in that case pure Ag_2S would be obtained.

XII. *Decomposition of Sulphuretted Silver Ores by Iron and Mercury.*

Since the discovery of the celebrated Comstock-lode in Nevada in 1859, enormous quantities of silver have been produced in that State and the adjacent States, Colorado, California, Utah, &c. The common pætio process not being applicable to the ores, which contain the silver especially chiefly as sulphide, and are mixed with pyrites, blende, and galena, a new and remarkable method, called the *Washoe process*, has been introduced to a great extent. The ores are ground with water in iron pans heated by steam, and mercury is added to form an amalgam. The theory of the process is very simple, the sulphide of silver being decomposed by the joint action of the iron and mercury.

I have convinced myself that Ag_2S, heated with iron powder, mercury and water, is in a short time almost entirely decomposed, while FeS is formed.

LIV.—*On Potable Waters.* (Part II.) *Determination of Total Solids.*

By Edmund J. Mills, D.Sc., F.R.S.

1. The determination of total solid matter in potable waters is a problem of extreme difficulty. The ordinary method of evaporation, followed by desiccation at 100° (or even at a higher temperature), necessarily leads, in nearly all cases, to chemical change in the very bodies which it is sought to estimate. Under these circumstances the following experiments may perhaps be of interest to analysts.

If a bulb, somewhat similar to the old-fashioned specific-gravity bead, but provided with a movable glass weight, be allowed to ascend in a saline solution of given strength, it will in general rise more slowly when more of the solvent is added. Assuming that the total solid matter in the strong solution is known, it is clear that we have thus at our disposal a mode of ascertaining the amount of any intermediate unknown dilution.

2. The bulbs and weights I have employed possess very nearly the external dimensions shown sectionally on half scale in the accompanying figure. The bulbs are constructed of lead glass, and are provided

externally with a few glass projections in order to keep them from accidental contact with a wetted surface. The water under examination is placed in a tall glass cylinder, preferably about 9 centimeters in diameter, and 33 centimeters high; on this are engraved, at points equidistant from the top and bottom, two lines 22 centimeters apart. Care must be taken to ascertain that the liquid is not evolving gas. By means of a small glass crook, the bulb with its attached weight is floated on the surface of the water; it is pushed down centrally, with the help of a smooth piece of quill-tubing, until the weight nearly touches the bottom. The tubing is then removed, and the time taken in the passage of the bulb between the two reference lines is counted by means of a metronome. It is necessary to work with scrupulously

clean surfaces, and at a constant temperature. Lateral wandering of the bulb does not occur after the operator has had a little practice.

3. The mathematical relations requiring to be taken into account in these experiments are comprised in the equation—

$$t(a + b\,S)^2 = c.$$

Of these symbols, t is the time, a is the unbalanced pressure, S the total solids, and b, c constants to be deduced from two experiments with the bulb. It is, however, better to make three dilutions at least, and calculate not only b and c, but a, from all of these. The symbols a, b, and c represent what may be termed the "constants of the bulb." For all moderate changes of strength in potable waters—at any rate, for a single water—the unbalanced pressure is a linear function of the total solids, and the relation above given will rigorously hold; in other cases it would require modification.

4. A method of this kind, depending upon unbalanced pressure, determines every constituent that is foreign to distilled water; but, in order to render it available, for one dilution at least the total foreign bodies should be known independently. This information can of course be approximated to in the ordinary way; but by far the best expedient is to determine the specific gravity. The Sprengel **U**-tube enables us to ascertain this, with much accuracy, to the fifth decimal place, the resulting number being very often directly related to the total foreign bodies, which are thus determined in their entirety, without decomposition.

5. *Series I.*—The water selected for experiment was Loch Katrine water, as supplied to Glasgow. Its sp. gr. at 9·2° (maintained throughout this series) was 1·000032. Now the "total solids," as ordinarily determined in this water, are very nearly 3 per 100,000; so that we may take the fifth and sixth decimals of the gravity (say 3·2) as accurately representing the total foreign bodies. Time was counted by means of a metronome beating thirds of seconds, and successive dilutions with distilled water were examined. The equation is—

$$t(0{\cdot}000140 + 0{\cdot}00000263\,S)^2 = 0{\cdot}0000021403.$$

TABLE I.

Loch Katrine water. per cent.	t.	S (by dilution).	S calc.
100	97·8	3·2	3·01
75	99·1	2·4	2·65
50	101·6	1·6	1·96
25	104·8	0·8	1·10
0	109·2	0·0	0·00

Probable error of a single experiment, 0·19.

6. *Series II.*—A watery solution was made containing calcium sul-

phate and sodium chloride nearly in the proportion $CaSO_4.2NaCl$. By direct evaporation, the total solid matter was found to be 52·24 parts per 100,000; the sp. gr. was 1·00051, which would correspond to 51 parts of "total solids." The temperature, bulb, and weight were the same as in Series I, but the cylinder was only 4·76 centimeters wide, in order to effect a slower ascent. The equation is—

$$t(0{\cdot}000140 + 0{\cdot}000001\,S)^2 = 0{\cdot}0000023066.$$

TABLE II.

Factitious water per cent.	t.	S (by dilution).	S calc.
100	63·8	51·0	50·1
75	71·6	38·2	39·5
50	84·2	25·5	25·5
25	99·1	12·8	12·6
0	118·2	0·0	− 0·3

Probable error of a single experiment, 0·55.

7. The experiments recorded above were all performed with the same bulb and weight. The rate of ascent, however, depends, not only upon the amount of solid matter dissolved, but upon the viscosity of the resulting resolution; and this is differently affected by different substances. Thus a solution of calcium chloride, containing 2·93 parts per 100,000 of that salt, gave an indication, under the previous conditions, of 8·00 parts; and a solution containing 29·3 parts per 100,000 of hydric sulphate apparently held 19·60 only. Again, a natural water of sp. gr. 1·0002458 at 9·3°, and yielding by evaporation 24·6 parts of "total solids," indicated 27·51 by the bulb method; and another natural water, of sp. gr. 1·000110 at 9·3°, yielding 9·5 parts of "total solids," showed 10·46 by the same method.

8. My experience, so far as it extends, is strongly suggestive of the following conclusions:—

(1.) The specific gravity of ordinary potable waters, and of other weak saline solutions, is a direct indication of "total foreign bodies per 100,000 parts."

(2.) This information having been obtained, the bulb method can always take its place in determining variations of strength in the same water, or solution; and the same "constants" may sometimes be available for different waters—probably for all very weak waters.

The bulb method will perhaps be of considerable service to those who are in the habit of estimating variations in the strength of potable water; and in such technical operations as brewing, where an intimate knowledge of the supply is indispensable. It will probably prove to be the readiest laboratory method for preparing standard solutions, and for detecting differences in the chemical con-

stitution of mixtures. The time consumed in applying it is extremely short. Thus, a natural water does not require more than a quarter of an hour's treatment to reduce it to the standard temperature; the subsequent operation with the bulb need not last more than half a minute.

LV.—*Chemical Examination of the Buxton Thermal Water.*

By J. C. Thresh, B.Sc.

The complete examination of any mineral spring includes (1) the analysis of the sinter or deposit formed by the water; (2) the examination of the gases held in solution, and of the gases evolved at the spring; and (3) the analysis of the water itself, to determine the nature and quantity of its organic and saline constituents.

The results of the 1st and 2nd series of analyses of the above spring I have now the honour of submitting to this Society, the 3rd series being reserved for a future communication.

The investigation was originally intended only to verify or disprove the remarkable statements made by Drs. Playfair and Muspratt, in their analyses, as to the quantity of nitrogen contained in this water; but after examining the mouth of the springs, and obtaining samples of the deposit, evidently of a peculiar character, a complete examination was decided upon.

The thermal water issues from several fissures in the limestone rocks, very near the edge of the mountain limestone formation (Robertson), at an elevation of about 1,000 feet above the sea level. The total outflow has been variously estimated at from 150 to 300 gallons per minute. The fissures or springs are all within a few yards of each other, and at the bottom of a closed reservoir, immediately over which is a large swimming bath, paved at the bottom with perforated marble slabs, fixed at a little distance apart, so that the water may be said to rise directly into this bath. On raising the slabs, which are supported on loose masonry, the springs can be seen, the principal one being apparently immediately under the centre of the bath; but although most water rises here, not much free gas accompanies it. The spring next in importance is close to one side, and here an almost constant stream of bubbles arises.

The under surface of these marble slabs is coated (or rather was coated before I removed the deposit) with a dark-brown mud, from one eighth to one quarter of an inch in thickness. Mixed with the

débris at bottom of the shallow reservoir, more of this mud could be seen, but not firmly attached to the stones as to the marble.

The temperature of the two springs just mentioned was taken by an accurately corrected maximum registering thermometer. The mean of three observations made at intervals of a few minutes gave 81·76° F. as the temperature of the entire spring, and 81·7° F. as that of the side spring.

1. *Analysis of Deposited Mud.*

This mud was collected by carefully scraping the slabs with a large knife. About as much as filled a 2—3 litre jar was obtained. Upon attempting to collect some from the bottom of the reservoir, the agitation caused it almost instantly to be diffused through the water, and carried away by the current.

A preliminary examination showed that this mud consisted chiefly of hydrated manganese dioxide, with small quantities of iron, zinc, cobalt, calcium, barium, and magnesium, and carbonic acid, together with traces of *molybdenum*, lead, copper, aluminium, strontium, and phosphoric, silicic, and sulphuric acids. After washing with distilled water, and drying in a water oven, it shrank up very considerably, leaving an exceedingly light, purple-brown powder, which stained the skin when rubbed between the fingers. Instead of about a kilogram of dry residue, as expected, the weight of the whole when dry did not exceed 50 grams.

Bunsen's, Marsh's, and other tests were applied for detection of arsenic and antimony, but no decided indication of the presence of either could be obtained. As molybdenum, so far as I am aware, has never before been found in any mineral water, the proofs of its presence in this spring are given in detail.

After evaporating the hydrochloric acid solution to perfect dryness, treating the residue with acid and water, a very small portion remained undissolved. The acid solution when heated to 70° C., and perseveringly treated with hydrogen sulphide, yielded a red-brown, finely pulverulent precipitate, which required about 36 hours to settle. This precipitate, when treated with potassium sulphide, partially dissolved, forming a reddish solution, which upon addition of dilute hydrochloric acid, yielded a red-brown, flocculent precipitate. Portions of this, exposed on a thread of asbestos to the reducing flame of a Bunsen's lamp, gave a slight brown stain on the bottom of a porcelain dish held immediately over it, which stain was insoluble in ammonium hydrosulphide and sodium hypochlorite, but soluble in nitric acid. The remainder of the dry precipitate and filter-paper was mixed with a little sodium carbonate and nitrate, added by degrees to fused

sodium nitrate, and the melt treated first with a little water, then with alcohol. A trace only remained undissolved. The solution acidulated with hydrochloric acid, gave with stannous chloride a brown coloration, and with potassium thiocyanate and zinc a rich crimson colour, unaffected by phosphoric acid, but taken up entirely by agitation with ether.

Another portion of the mud was exhausted with dilute nitric acid, and the acid solution was boiled with slight excess of sodium carbonate, and filtered. The concentrated filtrate gave with hydrochloric acid and with stannous chloride, and with hydrochloric acid potassium thiocyanate and zinc, the reactions of molybdic acid. After addition of ammonium hydrosulphide to this solution, excess of hydrochloric acid gave in a few minutes a distinct red-brown precipitate. To render if possible the evidence still more complete, at the request of Professor Roscoe, to whom I am indebted for many valuable suggestions in the course of this investigation, an attempt was made to obtain the very characteristic compound of phosphoric and molybdic acids with ammonia, from the molybdic acid obtained in the quantitative analysis. This attempt was successful, for upon dissolving the oxide in nitric acid, adding a little ammonia, then again nitric acid in excess, the yellow precipitate referred to was produced in a few minutes upon adding a minute trace of sodium phosphate, and warming the solution.

In the ammonium hydrosulphide precipitate, insoluble in dilute hydrochloric acid, nickel was sought for, but not detected. The barium chloride obtained when treated with absolute alcohol, gave up a very minute portion, in which, however, strontium could be detected by the spectroscope.

Hydrofluoric, tungstic, titanic, and boracic acids were specially tested for, but with negative results.

Quantitative Analysis of Mud dried at 120° C.

Loss on ignition. By ignition in a small table furnace—

0·7065 gram lost 0·1143 gram or 16·18 per cent.
0·5854 ignited over a blast-lamp lost 0·097 gram, or 16·57 per cent.
Mean loss 16·38 per cent.

CO_2. Estimated by aid of an apparatus constructed on a similar principle to that figured by Bunsen in his "*Instruction fur die Ausführung . . . Chemischen Untersuchung der Bädischen Mineralwasser*," and in the manner therein described.

3·8955 gram lost 0·1275 gram, or 3·27 per cent.
1·0631 „ 0·0339 „ 3·20 „
Mean 3·235 per cent.

MnO_2. The oxide was determined indirectly by ebullition with strong hydrochloric acid, the evolved chlorine being caused to liberate its equivalent of iodine, which was estimated volumetrically with standard solution of sodium thiosulphate.

0·3388 gram = 0·2587 gram MnO_2 or 76·36 per cent.
0·3160 „ = 0·2415 „ „ 76·42 „
Mean 76·39 per cent.

Portion insoluble in hydrochloric acid. 20·1411 grams when treated with excess of hydrochloric acid, evaporated to perfect dryness on the water-bath, then moistened with acid and treated with water, left a residue which after ignition weighed 0·2180 gram = 1·08 per cent. This residue was not quantitatively examined, but consisted of barium sulphate, fine sandy particles, &c.—(SiO_2, Fe_2O_3, Al_2O_3, BaO, H_2SO_4).

PbO. In the hydrogen sulphide precipitate, after treatment with potassium hydrosulphide until it was no longer coloured, the lead was estimated as sulphate by evaporating with sulphuric acid, dissolving the residue in nitric acid, washing with acidulated water, then with alcohol, drying, &c.

The lead sulphate weighed 0·0402 gram, corresponding to 0·147 per cent. PbO, and after treatment with potassium chromate, was entirely soluble in caustic potash.

CuO. From the concentrated filtrate from the lead precipitate the copper was deposited on a platinum dish by the action of pure zinc. The copper obtained weighed 0·011 gram, corresponding to 0·068 per cent. cupric oxide.

MoO_3. Upon adding dilute hydrochloric acid to the potassium hydrosulphide solution, a reddish precipitate fell which was dried upon a small filter. The paper was cut up and mixed with sodium carbonate and nitrate, and gradually added to fused sodium nitrate. The filtered aqueous solution of the smelt, after being neutralised with nitric acid, the carbon dioxide having been allowed to escape, was precipitated by mercurous nitrate, and the precipitate after some hours was collected, washed with solution of mercurous nitrate, dried, and ignited in a porcelain boat in a current of hydrogen.

The resulting MoO_2 weighed 0·003 gram = 0·016 per cent. MoO_3.

P_2O_5. After removal of hydrogen sulphide by evaporation from a portion of the solution which had been treated with that reagent, and corresponding to 1·7 gram deposit, excess of ammonia was added, then excess of nitric acid and some ammonium molybdate. The resulting precipitate, after many hours, was collected and treated with ammonia and magnesium mixture in the usual manner. The magnesium pyrophosphate obtained only weighed 0·0026 gram = 0·01 per cent.

CoO. To a portion of solution corresponding to 3·247 grams dry mud, ammonium chloride, ammonia, and slightly yellow ammonium hydrosulphide, were added in sufficient excess. After standing for 24 hours, the clear yellowish fluid was filtered off, and the precipitate rapidly washed with water containing a little ammonium hydrosulphide. In this precipitate the iron, aluminium, cobalt, and zinc were determined.

To isolate the cobalt, the precipitate was diffused through very dilute hydrochloric acid, and the mixture saturated with hydrogen sulphide. After filtering out the cobalt sulphide, the solution was reprecipitated by ammonia and ammonium hydrosulphide, and the precipitate again treated with dilute acid. The insoluble residue was digested with *aqua regia* (a minute portion, 0·002 gram barium sulphate was found here and estimated), evaporated to dryness in a porcelain dish, then boiled with slight excess of potash in a platinum vessel, and the well-washed precipitate was strongly ignited. Its weight was 0·0103 gram, corresponding with 0·30 per cent. CoO. The traces of Fe_2O_3 and alkali in this precipitate were not determined.

Fe_2O_3 and Al_2O_3. The filtrate from the cobalt sulphide was boiled with a little nitric acid, filtered, nearly neutralised with sodium carbonate, and the mixed ferric oxide and alumina were thrown down by ebullition with excess of $NaC_2H_3O_2$ solution. The slightly washed precipitate was redissolved, reprecipitated, ignited and weighed. The oxides, of which only a trace consisted of alumina, weighed 0·0440 gram = 1·36 per cent.

ZnO. The filtrates from the iron precipitate acidulated further with acetic acid and saturated with hydrogen sulphide, gave a nearly white precipitate of ZnS, which was collected, and dissolved in dilute hydrochloric acid; the solution was mixed with a slight excess first of sodium carbonate, then of acetic acid, and the zinc sulphide was reprecipitated. When converted into zinc oxide by strong ignition in an open crucible, it weighed 0·0150 gram = 0·462 per cent.

MnO. On account of accidental loss of some of the solution, the manganous oxide had to be determined from a fresh portion of the deposit, after removal of the oxides of lead, copper, cobalt, and zinc, and of the ferric oxide, alumina, baryta, lime, and magnesia. The manganese was precipitated by ammonia and ammonium hydrosulphide, washed, dried, and ignited in a current of hydrogen. From 0·9061 gram deposit 0·7316 gram manganous sulphide was obtained, corresponding to 66·19 per cent. MnO, or 71·11 per cent. Mn_3O_4. From estimation of MnO_2, the amount of oxygen united with the manganese over and above that required to form MnO, is found to be 14·13 per cent., or 9·21 per cent. more than would convert the whole into Mn_3O_4.

Water of Hydration.—Found by deducting from the total loss upon ignition, the amount of CO_2 and O which would be driven off—

$$16{\cdot}38 - (9{\cdot}21 + 3{\cdot}24) = 3{\cdot}93 \text{ per cent.}$$

BaO. The filtrate from the ammonium sulphide precipitate, of solution in which zinc, iron, &c., had been estimated, was boiled with hydrochloric acid, filtered, rendered slightly alkaline with ammonia, and the calcium, barium, and trace of strontium thrown down by addition of ammonium oxalate to the hot solution. After reprecipitation and intense ignition, the mixed oxides weighed 0·1969 gram.

This residue, after treatment with nitric acid and evaporation to dryness, was digested with absolute alcohol. After 24 hours, the thick liquid was filtered off, and the residue washed with more alcohol, then dissolved in water, evaporated to dryness in a platinum dish, and weighed. Its weight was 0·0416 gram, corresponding to 0·788 per cent. BaO (corrected for $BaSO_4$ found in CoS precipitate).

CaO. Deducting the amount of BaO corresponding to 0·416 gram $Ba(NO_3)_2$, we have 0·1725 gram CaO = 5·31 per cent.

MgO. The filtrate from the calcium and barium precipitates was evaporated to dryness, gently ignited, and the magnesia determined after reprecipitation as $Mg_2P_2O_7$. This salt weighed 0·2864 gram = 3·178 per cent. MgO.

The results of the analysis are tabulated below, expressed to the nearest second decimal:—

Mn_3O_4	71·11
O	9·21
$BaSO_4$ and other matters insoluble in hydrochloric acid	1·08
PbO	0·15
CuO	0·07
MoO_3	0·02
CoO	0·30
$Fe_2O_3 + Al_2O_3$	1·36
ZnO	0·46
BaO	0·79
CaO	5·31
SrO	a trace
MgO	3·18
CO_2	3·23
P_2O_5	0·01
H_2O	3·93
	100·21

It will be noticed that this deposit corresponds closely in composi-

tion with that of many samples of psilomelane, and wad or bog manganese.

2. *Analysis of the Gases.*

The gases at the side spring were collected as described by Bunsen in the work previously mentioned, the small flasks being closed with perforated caoutchouc stoppers fitted with tubes, &c., as figured in Bunsen and Roscoe's "Gasometry," and then inverted in glass cylinders containing sufficient water to cover the necks.

Arrived in the laboratory, the gas was transferred as required to the absorption-tube, and the CO_2 determined by absorption with balls of fused potash. The residual gas, after treatment with a papier maché ball impregnated with alkaline pyrogallate, was inappreciably affected; it contained no combustible gas, and, in fact, comported itself in every way as pure nitrogen.

The analyses 1 and 2 were made from the same sample of gas; 3 and 4 from another sample which had stood for a while in a flask in which by accident a little of the water had been left. Several other analyses were made of gas collected in the bath, the results in all cases falling between the means of 1 and 2, and 3 and 4.

The pressures and volumes given refer to the dry gas. All readings were taken by aid of a telescope sliding on a vertical support.

Gas collected March 22nd, 1881, *at Side Spring.*

	Vol.	Pressure.	Temp.
(1.) Gas taken	43·01	693·9	8°
After absorption of CO_2 ..	42·08	696·7	5·4°
Giving N	99·161		
CO_2	0·839		
	Vol.	Pressure.	Temp.
(2.) Gas taken	42·28	687·8	5·9°
After absorption of CO_2 ..	41·28	696·5	5·3
Giving N	99·083		
CO_2	0·917		
	100·00		
	Vol.	Pressure.	Temp.
(3.) Gas taken	42·73	709·7	5·3°
After removal of CO_2	41·96	711·7	4·8
Giving N	98·65		
CO_2.....	1·35		
	100·00		

	Vol.	Pressure.	Temp.
(4.) Gas taken	31·40	653·2	12·5°
After absorption of CO_2 ..	30·12	668·4	11·2

Giving N	98·61
CO_2	1·39

The mean of two experiments made by Playfair in 1852, gave 1·167 as the percentage of carbon dioxide.

The gas, if allowed to stand in contact with a little of the mineral water, will become richer in carbon dioxide, since, as will presently be seen, the nitrogen and carbon dioxide exist in the water in much more nearly equal proportions, and under a pressure of about 1·6 atmospheres. Hence upon removal of the pressure the evolved gas will become richer in carbon dioxide, and the greater the depth (and therefore pressure) at which the gas is collected, the less carbon dioxide will it contain. The slight variations between my analyses 1 and 2, and Playfair's may possibly be due to this cause.

3. *Gases Dissolved in the Water.*

On account of my mercury trough not being sufficiently large to permit of the transfer of gases from a long tube into the absorption-tube, the gases evolved upon ebullition of the water were collected and transferred by what may be called a modification of Reichardt's method, which was found both convenient and trustworthy, and will afterwards be described.

A number of examinations were made of the water from the spring and from the bath, and in all cases the flasks, after being filled with the water, were taken directly into the laboratory (only about 200 yards distant), and in the nitrogen determinations connected at once with the gas-receiving apparatus and the analysis proceeded with.

The flasks employed for collecting the water varied in capacity from 300 to 700 c.c., as when the bath is run off there is but just sufficient water in the reservoir below at the mouth of the springs to allow of such flasks being fully immersed.

After being well rinsed with the water, the bottles were filled with it, put as far as possible into the crevices through which the water rises, and, by aid of a syringe, the water they first contained was displaced by that from the greater depth. Whilst still in this position they were stoppered with well-kneaded rubber corks perforated with one hole and plugged with a short piece of glass rod. The weight and density of the water being known, the volume used for each analysis was easily found. In filling the flasks at the bottom of the bath, they were weighted, sunk, the water displaced by the action of the pump,

the tube of the latter withdrawn, and a rubber stopper fixed at end of a long rod carefully inserted. The flasks were then drawn to the surface. Great care had to be taken in these operations, as the slightest movement in the water causes a disengagement of gas. Agitation with the hand gives rise to a number of minute gas bubbles, rendering the water turbid for a few moments.

N. To obtain all the nitrogen, the water was boiled under diminished pressure for from $1\frac{1}{2}$ to $2\frac{1}{2}$ hours, and, after collecting the evolved gas in an absorption-tube, bullets of fused potash were passed in until all the CO_2 and moisture were removed. Whenever the gas was afterwards treated with alkaline pyrogallate, a trace of oxygen was found, but from its small proportions and from considerations derived from the composition of the deposit, no doubt its presence was due to traces of air entering the apparatus during the analyses.

CO_2. To determine the carbon dioxide, 100 c.c. of water taken up by aid of a pipette connected with a syringe sunk as far as possible, were transferred to a flask containing 10 c.c. of a solution of sal-ammoniac and calcium chloride, and 50 c.c. of lime-water of known strength immediately added. After standing for about 24 hours, 50 or 100 c.c. of the clear fluid were removed and titrated with dilute nitric acid, of such strength that 1 c.c. = 1 mgrm. CO_2. The precipitate of calcium carbonate was as far as possible collected on a filter, washed, and the filter and contents returned to the carefully-rinsed flask. After treatment with a measured excess of dilute acid, and gentle ebullition, the acid solution was titrated back with lime-water.

In one or two instances 250 c.c. of the thermal water were employed for determination of the carbon dioxide.

1. *Water taken from Side Spring, April 14th*, 1881. *Vol.* 0·707 *litre at* 81·7° F.

Residual gas after	Vol.	Pressure.	Temp.
Absorption of CO_2 ...	19·05	614·5	5°
After absorption of O.	18·80	614·9	2·9°

Total CO_2 0·1901 gram; free, and as bicarbonate, 0·1096 gram; free CO_2 0·0291 gram, or 14·76 c.c.

1 litre of water would therefore contain—

N	21·30 c.c.
CO_2	14·72 „
O	a trace
	36·02

(2.) *Water taken March 22nd, 1881. Vol. 0·385 litre.*

CO_2 free gas	11·77 c.c.	584·2	6·2

Total CO_2 per litre, 0·1939 gram; free, and as bicarbonate, 0·1122; free, 0·0305 gram, or 15·43 c.c.

Giving per litre of water—

N	22·98
CO_2	15·43
	38·41

3. The mean of four nitrogen and carbon dioxide determinations in water taken from the bath, gave—

N	22·04 c.c.
CO_2	14·50 „
	36·54 „

The composition of the dissolved gas per cent. may be taken as mean of above results.

	(1.)	(2.)	(3.)	Mean.
N	59·13	59·83	60·38	59·78
CO_2	40·87	40·17	39·62	40·22

The theoretical composition of the gas evolved at the spring, as calculated from the mean of these analyses of the gas held in solution, is—

N	98·98
CO_2	1·02

found from equation—

$$\frac{100 \times 0{\cdot}01392 \times x}{0{\cdot}01392x + 0{\cdot}9054\,(100 - x)} = 59{\cdot}78,$$

where x = per cent. of nitrogen in the gas evolved.

The proportions found by actual experiment agree as closely as could be expected with the above result—

		Playfair.
N	99·12	98·83
CO_2	0·88	1·17

To charge pure water with the amount of gas found in the Buxton thermal water would require a pressure equal to that of 1·12 meters of mercury, the temperature of the water being 81·7° F. The normal atmospheric pressure at the springs being 736 mm., the water may be said to issue from the earth charged under a pressure of 1·64 such atmospheres.

Playfair, in the report made in 1852, and published in various Journals and in Robertson's "Guide to Buxton and the Peak," has the following paragraph :—

"Judging from the analysis and proportion of the gases, it is assumed that, at the moment of issue, the water is charged with 206 cubic inches of nitrogen and 15·66 cubic inches of carbonic acid. This assumption is founded upon the proportional relation of the two gases. The proportion of carbon dioxide in the water being determined, and the proportion of this gas to that of nitrogen contained in the water being 1·2 to 98·8, the amount of nitrogen contained in the water at the moment of issue may fairly be assumed to be 206 cubic inches per gallon."

As he had found 3·47 cubic inches of *free* carbon dioxide in one gallon of the water, and $\frac{3{\cdot}47 \times 98{\cdot}8}{1{\cdot}2} = 286$, this latter number should, according to Playfair's reasoning, represent the number of cubic inches of nitrogen in that quantity of water.

This analysis was completed before Bunsen and Roscoe's "Gasometry" was published, but, so far back as 1806, Dalton had treated on the laws affecting the absorption of gases by water, and evidently at the time of writing Playfair had entirely forgotten these researches.

Muspratt (*Dict. of Chemistry*, Edit. 1, 1098) affirms, from the result of an analysis made in 1860, that each gallon contains—

CO_2	3·5	cubic inches.
N	504·0	„

He then adds: "Dr. Robertson in treating of the physical characters of the Buxton waters, ascribes their brilliancy when drawn to the *gas held in solution*. Of course this must be fallacious, for very little gas is *held in solution or dissolved*." A most remarkable statement, certainly: one would infer from it, that in his report 5·04 and not 504 cubic inches were intended, but, that such is not the case is evident from the fact that (*ibid.*, 1082) in discussing the source of the nitrogen he writes: "With so unnatural a phenomenon, the question, Whence does it come? at once intrudes itself. That it is assimilated from the air is impossible; and it is hardly conceivable that the water in passing through the calcareous strata of the district should meet with or take up such quantities of nitric acid and ammonia as would by their mutual decomposition in some such manner as the following—

$$3NO_5 + 5NH_3 = 15HO + 8N,$$

give rise to the aforenamed volume of gas." And again (fol. 1097), he adds: "Annexed is an analysis of the Buxton water just completed by the editor; it differs materially from the one made by his friend Playfair some time ago, *except in the amount of gases*."

How Muspratt arrived at his conclusion as to the enormous quantity of nitrogen in the water, he does not state; neither does he bring forward any hypothesis as to the condition in which the nitrogen exists in the water, though he says it is not dissolved.

The constitution of the mud deposited by the spring appears to me to throw some light upon the origin of the nitrogen, and to account for the absence of oxygen. Thus, supposing the water at its source to become charged with air under some little pressure, and afterwards to traverse a bed of manganese ore capable of taking up oxygen, the whole of this gas would disappear. The fact that the moist deposit when exposed to air does take up oxygen, is a proof of the absence of that gas in the free state in the water.

Briefly summarised, my results prove conclusively that this water is surcharged with gas, containing in the bath and reservoirs as much as could be forced into it by a pressure of 1·64 atmospheres; that the gas evolved at the spring is nearly pure nitrogen, containing, in fact, only 1 per cent. of carbonic acid and no oxygen.

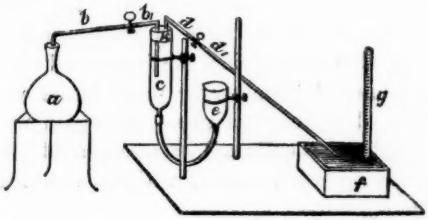
The character of the deposit is interesting, both on account of its containing a trace of molybdenum, and as affording an explanation of the total absence of oxygen in the water, thus rendering it probable that originally the nitrogen was derived from the atmosphere, since the bulk of the deposit consists of oxides of manganese still capable of taking up a further proportion of oxygen.

LVI.—*Modified Form of Apparatus for Collecting the Gases Dissolved in Water.*

By J. C. Thresh, B.Sc.

In making a series of nitrogen determinations in the Buxton thermal water, I was led to devise a form of apparatus which proved to be convenient for use, and to give very uniform results.

The following figure will illustrate at once the construction and mode of using the apparatus:—



a is the flask containing the water to be examined; *b* and b_1 two pieces of thermometer tubing connected by a short length of caoutchouc tubing carrying a pinchcock; *c*, a cylindrical glass tube drawn out at its lower extremity, and by aid of a long piece of stout caoutchouc tube joined to the similar but much wider vessel, *e*, both being attached by clamps to upright supports; *d* joined to d_1 by rubber tubing, and carrying a pinchcock, serves to transfer gas from *c* to the absorption-tube, *g*. *c* is closed by a firm rubber cork with two perforations, one traversed by b_1, which terminates about middle of *c*, and the other by *d*, which barely passes through the stopper.

When a determination is to be made, the flask, after filling at the well with the usual precautions, is closed by a stopper of rubber perforated at the centre, the lower end of the opening being securely plugged by a short piece of glass rod. *e* is lowered, filled with mercury, then raised until *c* also is filled, when the stopper *k* with its fitted tubes is firmly inserted. On raising *e* still higher and opening the two pinchcocks, the tubes *b* and b_1, *d* and d_1, are completely filled with mercury, a little manipulation being sometimes necessary to drive all the air from the parts where the tubes are connected. The pinchcocks being closed, *e* is now lowered as far as possible and left in this position for some time, when, if no air-bubbles have made their appearance, the experiment can be proceeded with. The free end of *b* is now inserted into the orifice in the stopper of the flask containing the water (care having been taken previously to replace any air or water in the cavity by mercury, and to see that the tube *b* is quite full of that metal), and gently pushed down so as to force the plug into the bottle, and until the end of the tube can just be seen below the stopper.

On now releasing the clamp upon *b* b_1, and applying heat to the flask, the heat and diminished pressure cause the gas to be readily given off, and ultimately the water will boil at a temperature below 100°, depending of course upon the difference between the levels of the mercury in *c* and *e*. The expansion of the water causes a portion to pass into *c*, above which the evolved gas collects, and when the latter nearly half fills the tube, *e* is raised after opening the pinchcock on *d* d_1, and most of the gas thus forced into the absorption-tube. This process can be repeated as often as necessary, care being taken not to force any mercury into the water flask, or any water into the tube *d* d_1, and to keep the end of the tube b_1 always under the surface of the fluid in *c*. Finally, by keeping *e* raised until the water is nearly at 100°, and then lowering, the water in *c* may be made to boil and give up almost the last trace of gas. On again raising *e*, &c., the whole of the evolved gas is collected in *g*, saturated with moisture, but, due precaution having been taken, without any trace of water on the surface of the mercury.

The capacity of c may vary according to the richness of the water gaseous constituents, but will chiefly depend upon the quantity of water used, as when much gas is present it can readily be transferred from time to time into g. For flasks of from $\frac{1}{2}$ to 1 litre capacity, c should be capable of holding at least 100 c.c.

LVII.—*On the Sulphides of Copper.*

By Spencer Umfreville Pickering, B.A. Oxon, Assistant Master at Highgate School; Lecturer in Chemistry at the Bedford College.

University of Michigan

Having had occasion to heat some cupric sulphide for some time in a current of hydrogen, I was surprised to find that a partial reduction to metallic copper had taken place, although it was considered as a well ascertained fact that the reduction in hydrogen did not proceed further than cuprous sulphide. An investigation of the subject was consequently made, the results of which, as detailed in the present paper, tend to throw considerable doubt, if, indeed, they do not entirely disprove the correctness of the formula CuS for cupric sulphide.

I. *Sulphides Used.*

A. *Cupric Sulphides.*—The cupric sulphides used were obtained by three different processes.

(1.) By the precipitation of cupric sulphate obtained from electrotype copper by hydrogen sulphide, and drying the sulphide thus obtained in a current of that gas at a low temperature. The following numbers were obtained on analysis:—

	Found.	Theory.
Cu.....	66·379	66·41
S	33·601	33·59
	99·980	100·00

(2.) By heating electrotype copper with strong sulphuric acid at 180° C. for 30 minutes (see *Chem. Soc. J.*, 1878, 117). The specimen thus prepared was quite free from cuprous sulphide, as shown by analysis, but contained some free sulphur, which was expelled on heating it for a short time at 160° in a rapid current of hydrogen. It gave by analysis the following numbers:—66·29 per cent. copper, and 33·56 sulphur.

(3.) Attempts were made to prepare some copper sulphide by heating a solution of copper sulphate with one of sodium thiosulphate, and then boiling the liquid according to the directions of Rammelsberg (*Pogg. Ann.*, **56**, 321). In the first case, however, different portions of the product thus obtained were found to yield the following results on analysis:—57·588, 65·941, 61·716, and 60·914 per cent. copper. These numbers show that the product is not uniform in composition, but is a mixture of cupric sulphide (which contains 63·644 per cent. Cu), and some more or less oxidised compound. A second preparation was made in the same way, and dried in a current of carbon dioxide: it was found to contain 63·6 per cent. of copper, showing it to consist of cupric sulphide alone; but after being kept for some time in air, or heated in air at 100°, it was found to have undergone a slight amount of oxidation, and was therefore used in only very few of the following experiments.

All these cupric sulphides possessed a green colour to a greater or less extent, which has been already shown not to be due to the presence of sulphate (this Journal, 1880, 115). Many specimens prepared by precipitation with hydrogen sulphide were found to undergo gradual oxidation in the air, but the only one used in these experiments remained perfectly unchanged throughout the course of the investigation.

B. *Cuprous Sulphides.*—Two specimens of cuprous sulphide were prepared as follows.

(1.) By heating electrotype copper with strong sulphuric acid for 30 minutes at 124°. In this way a specimen was obtained quite free from cupric sulphide (see *ibid.*), as was proved by its evolving no hydrogen sulphide on being heated at about 300° in a current of hydrogen (see § III). The following numbers were obtained on analysis:—

	Found.	Theory.
Cu	79·763	79·814
S.....	20·216	20·186
	99·979	100·000

(2.) By the reduction of cupric sulphide in a current of hydrogen in the manner which will be described below.

Both these specimens of cuprous sulphide were black powders containing no trace of sulphate, and remaining quite unoxidised on exposure to the air for an indefinite time, either at ordinary temperatures or at 100°. The first-mentioned sample, which was prepared by the wet process, could also be dried at 100° without suffering any oxidation.

II. *Method of Experimenting.*

In experiments in which temperatures no higher than 300° were required, the sulphide to be examined was placed in a small **U**-tube, one limb of which was drawn out very fine. The heating apparatus which was finally adopted as being most convenient, was a double air-bath of stout iron in the form of a glue pot. The temperature here could be maintained pretty constantly within 5° or 6° on either side of any particular point. When a higher temperature was required, the sulphide was heated in a porcelain boat placed in a porcelain tube in a Hofmann's furnace.

When hydrogen was employed in these experiments, it was purified and dried by being passed first through a solution of silver nitrate, then through a mixture of potassium bichromate solution and sulphuric, and subsequently calcium chloride and sulphuric acid sufficient to expose a drying surface of about 5 feet in length. The absence of any oxygen in the hydrogen thus obtained was satisfactorily proved. Where carbon dioxide was used instead of hydrogen, a somewhat similar drying apparatus was employed, but, in spite of various precautions, it was not found possible to free this gas entirely from traces of oxygen.

III. *The Sulphides Heated in Hydrogen.*

Some of the cupric sulphides (1) and (2) were heated in a slow current of hydrogen, using the heating apparatus first described, and raising the temperature very gradually; the issuing gas passed over blotting paper moistened with lead acetate, and if this remained quite unstained during 30 minutes while the temperature of the bath was constant, it was concluded that no hydrogen sulphide was formed at this temperature.

The actual temperatures at which hydrogen sulphide was first observed were, in the case of sulphide (1), 200°, 197°, and 204°; in that of the second specimen (2) they were 205° and 199°, while one experiment made on the somewhat impure sulphide (3) gave the temperature 195°. Hence in these three different cases, the temperature of initial action is within the errors of observation the same, being about 200°.

After having observed this temperature, more heat was supplied till the thermometer stood at or near 265°, which temperature was maintained throughout most of the experiments. The temperature was occasionally lowered and then raised again in order to ascertain whether the temperature of initial action still remained the same, and it was invariably found that it did so remain till the last trace of hydrogen sulphide had come off, which would be given off below a red

heat. The contents of the tube were then weighed, with the following results:—

	Wt. of CuS taken. gram.	Wt. of Cu_2S obtained. gram.	Theory. gram.
1.	0·1814	0·1506	0·1509
2.	0·0680	0·0561	0·0566
3.	0·0644	0·0536	0·0536
4.	0·1533	0·1280	0·1275
5.	0·1030	0·0850	0·0857

The first three experiments were performed with the sulphide (1), and the last two with the sulphide (2). Unfortunately only small quantities of material could be used on account of the action being extremely slow, about 60 hours' heating at 265° being necessary to reduce each 0·1 gram of cupric sulphide to cuprous sulphide. Still, however, the above experiments can leave little doubt that hydrogen at this temperature does reduce cupric sulphide exactly to cuprous sulphide and no further.

On gradually raising the temperature of the air-bath after the sulphide had been reduced as far as it could be at 265°, no more hydrogen sulphide was evolved till a red heat had nearly been attained: the actual temperature at which this second evolution began was determined by means of an air thermometer placed inside the porcelain tube. The temperatures thus indicated are only approximations; with the cuprous sulphide (1) 650° and 580°; with (2) 620° were observed. After the action had continued for a short time at these or somewhat higher temperatures, particles of metallic copper were observed in the sulphide, and after the action had been continued long enough, the whole was found to be reduced to metal, while throughout the reduction the temperature of initial action appeared to remain constant. The following numbers are some out of many of those which were obtained:—*

	Wt. of Cu_2S taken. gram.	Wt. of Cu obtained. gram.	Theory. gram.
6.	0·2135	0·1704	0·1704
7.	0·1801	0·1435	0·1437
8.	0·1506	0·1243	0·1245
9.	0·1814	0·1450	0·1448
10.	0·0536	0·0443	0·0442

These numbers show that cuprous sulphide may be reduced entirely

* With the quantities of material here used the hydrogen occluded by the copper would not sensibly affect its weight.

to metallic copper by heating it in hydrogen; indeed, the reduction is so complete and accurate, that when the apparatus required was in readiness, it was found to be the quickest and, at the same time, the most exact method of estimating the copper in a sample of its sulphides. Rose's (*Pogg. Ann.*, **110**, 138) method for estimating copper by the ignition of its sulphide with sulphur in a current of hydrogen which, according to himself and also Fresenius, yields very trustworthy results, would lead one to suppose that cuprous sulphide is not attacked by hydrogen; yet the explanation of this may perhaps be that, in an analysis according to Rose, the sulphide is not ignited sufficiently long nor at a sufficiently high temperature to allow an appreciable amount of reduction to take place; in addition to which he starts by having a large amount of sulphur present, which must be entirely driven off before any reduction can begin at all. Indeed, although the temperature of initial action of cuprous sulphide and hydrogen is not very high, still the action is by no means rapid: thus, at the highest temperature producible in the Hofmann's furnace, the average time required was about five hours for each 0·1 gram of cuprous sulphide taken.

These experiments, therefore, show that cupric sulphide when heated in hydrogen gives up its sulphur in two equal portions, the first portion being removed at 200°, while the second portion is not given up till about 600°; it also appears that the temperature of initial action does not differ very much in the different specimens of sulphide here employed; the determinations of these temperatures, however, have no pretensions to accuracy.

IV. *The Sulphides Heated in Carbon Dioxide.*

These experiments were conducted in a manner precisely similar to that above described, except that carbon dioxide was substituted for the hydrogen. To ascertain whether any action was taking place, the issuing gas was made to impinge on a small piece of blotting-paper moistened with the solution of iodic acid and starch, the sulphur dioxide being thus easily detected by its liberation of iodine. In the case of the cupric sulphide (1) prepared by precipitation with hydrogen sulphide, the temperature of initial action was found to be 131°; with the sulphide (2) the temperature observed was 115°, but some doubt exists as to the accuracy of this latter determination.

In the following experiments weighed portions of the precipitated sulphide were heated in a current of the gas at 130—150°. After many hours at this temperature, the evolution of sulphur dioxide ceased, and no more was evolved by increasing the heat up to 200°.

The weights of the residual sulphides thus obtained were as follows:—

	Wt. of CuS taken. gram.	Wt. of Cu_2S obtained. gram.	Theory. gram.
11.	0·08435	0·0702	0·07015
12.	0·13050	0·1083	0·1085

and these show that, as in the case where hydrogen was used, the product obtained is cuprous sulphide. No oxidation could be detected as having taken place.

On the temperature being further increased to about 230°, a further evolution of sulphur dioxide began, and, after a short time, particles of metallic copper made their appearance. When the heating had been continued for some time at 300 to 350°, the whole was found to have been completely reduced to metallic copper, except that the particles of metal were coated with a little oxide sufficient to give them a red appearance, owing no doubt to the traces of oxygen present in the carbon dioxide as above mentioned. The following numbers were obtained:—

	Wt. of CuS taken. gram.	Wt. of Cu obtained. gram.	Theory. gram.
13.	0·08435	0·0561	0·05595

No phosgene or carbon disulphide was detected as being formed during the action.

Here, then, as in the case where hydrogen is used as the reducing agent, the sulphur in cupric sulphide is abstracted in two equal portions at two different temperatures, and the initial temperature of each action remains the same throughout its duration.

V. *Evolution of Sulphur from Cupric Sulphide by Heat alone.*

When cupric sulphide is heated to a sufficiently high temperature, even in a gas which has no reducing action upon it, it gives off half of its sulphur; this sulphur is liberated in a similar manner when the sulphide is heated in a gas which has only a slow action upon it.

Some of the precipitated sulphide (1) was heated in the **U**-tube in the air-bath while a rapid current of hydrogen was passed over it; on gradually raising the temperature, it was found that traces of sulphur first made their appearance in the cool part of the tube at 293°, and that, after the heating had been continued at 320° to 330° for about ten hours, no more sulphur was volatilised; after which the residue consisted entirely of cuprous sulphide. The following numbers were obtained:—

	Wt. of CuS taken. gram.	Wt. of Cu_2S obtained. gram.	Theory. gram.
14.	0·0934	0·0797	0·0777
15.	0·0767	0·0754	0·0754
16.	0·1321	0·1096	0·1099

VI. *Theoretical Bearing of these Experiments.*

But one conclusion can be drawn from the facts detailed above. Under the influence of three different agents cupric sulphide parts with its sulphur, but it does not part with it all at once; it is given off in two separate and equal portions and at totally different temperatures. The sulphur is removable in two equal portions, and therefore the molecule contains two atoms of sulphur.

In the case where heat alone is the reducing agent, it might be argued that all the sulphur is in the first instance given off, but that half of it immediately recombines with the metal to form the cuprous compound. The improbability, however, of such an action taking place, renders it scarcely worthy of discussion, especially as in the other cases no such objection can be raised; for, taking the case where hydrogen is used as the reducing agent, we can hardly imagine that the whole of the sulphur is first converted into hydrogen sulphide, and that this latter then reacts with the reduced copper to form the cuprous sulphide, for this view would be equivalent to saying that an element (copper) may be liberated in a medium (hydrogen sulphide) which reacts on it, and in which it is incapable of existing;* nor can we suppose that one molecule of the cupric sulphide is entirely reduced, and that the atom of copper thus liberated at once combines with a contiguous unreduced molecule of the sulphide; for, in addition to other objections, this would involve chemical combination taking place between two perfectly stable non-volatile solids at a temperature very many hundred degrees below their fusing points. We can obtain no explanation of the observed facts but that the molecule of cupric sulphide contains two atoms of sulphur, and that its formula is Cu_2S_2, and not CuS, as it has hitherto been assumed to be.

Experiments similar to those above described were commenced on the oxides of copper, but before they had been proceeded with very long, a publication by Dr. Wright appeared (*Chem. Soc. J.*, 1878, 1), which showed that the temperatures of initial action of hydrogen on the two oxides of copper were too nearly identical to render any success with them at all probable.

In these experiments on the sulphides of copper, and also in some

* There can be no question of dissociation here.

more numerous, but yet unpublished ones, on the sulphides of iron, the general results obtained indicated that in any particular case the temperature of initial action was independent of the physical state of the substances examined, there being no question here of allotropic modifications. The subject of initial temperatures, however, was neither investigated with great care nor for its own sake, but merely as an outcome of the main question; but at any rate, it served to show that the metallic sulphides were particularly well adapted for an investigation on this point; for, in the case of hydrogen, for instance, an action which may continue for many hours without producing an appreciable loss in weight, will yet produce sufficient hydrogen sulphide to be detected with lead paper in the course of a minute or two. The experiments of Wright, which indicate that the temperature of initial action is influenced by the physical condition of the reagents, can, in my opinion, scarcely be considered to have settled the question. It is surely not "highly probable, *a priori*," that a chemical action taking place between the same two chemical compounds should begin at different temperatures, according as one of those compounds is more compact or more finely divided, or, generally speaking, in a different physical condition; surely it is equally probable, and perhaps more probable, that this difference in physical condition would not affect the temperature of initial action, but only the rate at which that action proceeds; nor can we conclude that the fact of no estimable action having been observed at some particular temperature during the course of 15 minutes absolutely proves that no action whatever was taking place at this temperature. The question, as far as I can see, could receive a satisfactory solution only by determining the amount of action taking place at various temperatures, and calculating the temperature of initial action from the curves obtained from these experiments.

It would have been interesting to ascertain whether the rule which Wright found to hold good in the case of the oxides of copper and other metals, "that the greater the heat disturbance in any particular action, the lower the temperature at which that action begins," held good in the case of the sulphides of copper also; unfortunately, however, no determinations of the heat of formation of cuprous sulphide exists, so that this point must for the present remain unsettled.

LVIII.—*On the Isomeric Acids obtained from Coumarin and the Ethers of Hydride of Salicyl.*

By W. H. Perkin, F.R.S.

Some time since I published an account of two isomeric methylorthoxyphenylacrylic acids, which I designated as α and β. The former is prepared by treating the compound of coumarin and sodic hydrate with methylic iodide, by which means either its saline compound or methylic ether can be obtained (*Chem. Soc. J.*, 1877, 417—420); the latter, by heating the hydride of methylsalicyl with acetic anhydride and sodic acetate (*Chem. Soc. J.*, 1877, 414). It will be remembered that these acids differ from each other very widely, the fusing points being about 90° C. apart. The most remarkable fact, however, is that by the action of heat the α-acid becomes converted into the β.

The cause of the isomerism of these bodies being unexplainable—their formation indicating that they should be identical—it was hoped that by studying their properties and derivatives side by side, and preparing, if possible, some of their homologues, some light might be thrown on this subject.

To render the consideration of the results I have obtained as clear as possible, I have thought it best first to give an account of all the products that have been obtained, together with their analyses, and afterwards to consider their bearing and relationship to each other.

α-Methylorthoœyphenylacrylic Acid.

To purify this acid it has been found useful to crystallise it first from petroleum spirit, in which it is only moderately soluble, and then once or twice from alcohol. It is very soluble in this fluid, and does not crystallise out from it for some time. However, it then forms large magnificent crystals, which refract light like jewels whilst in their mother-liquor, but lose their lustre when removed, as some of the solution dries on the face of the crystals, and renders them dull. This acid also crystallises very well from carbon bisulphide. The crystals belong to the oblique system. Their measurements are given at the end of this paper.

I have already referred to the change which this acid undergoes when heated, whereby it is converted into its isomeride the β-acid. Experiments have also been made with light, which is found to act in a similar manner, a strong alcoholic solution, when exposed to the

sun, soon depositing crystals of the β-acid. The fused acid also changes in a similar manner when the light is concentrated upon it.

To see which rays of light caused this change, test-tubes containing strong solutions of the acid were immersed in variously coloured solutions contained in bottles, a solution of sulphate of quinine, and to make the experiments comparative, water was also taken. After exposure to light for some time, crystals of the β-acid were formed in the tubes immersed in water and in the blue solution (ammoniacal sulphate of copper), all the others were apparently quite unacted upon. The quinine solution also prevented any change from taking place, so that it is evident that the alteration is due to the action of the violet and ultra-violet rays.

If α-methylorthoxyphenylacrylic acid be boiled with dilute hydrochloric acid, it melts, and nothing appears to occur for some time, when it rapidly becomes crystalline. On recrystallising this from alcohol two or three times, it gave on analysis numbers showing that it had not changed in composition. The fusing point, however, had risen to 178°; therefore it evidently had been converted into the β-acid; other acids, as dilute sulphuric acid, also induce this change.

Baric α-Methylorthoxyphenylacrylate.

The above acid easily dissolves in a boiling solution of baric hydrate, forming a pale-yellow solution. After removal of the excess of baric hydrate by carbonic acid, the solution may be concentrated, until somewhat syrupy, without depositing the salt, and on standing for a day or more may remain clear, and then suddenly become a crystalline mass. After a time this changes, and the small crystals which filled the liquid are replaced by rather large transparent ones of a pale-yellow tint.

A barium determination of the salt dried at 100° gave the following result:—

0·2460 of substance gave 0·1147 of $BaSO_4$ = 27·41 per cent. Ba.

The formula $C_{20}H_{18}BaO_6$ requires 27·26 per cent. of Ba.

Methylic α-Methylorthoxyphenylacrylate.

The preparation of this ether has previously been given (*Chem. Soc. J.*, 1877, 418). I find, however, that the digestion of the compound of sodic hydrate and coumarin with methylic iodide and alcohol should not be continued longer than necessary. I generally heat the mixture in a soda-water bottle securely corked and placed in a water-bath, kept at 100° for about three hours. If the digestion be carried on, say for eight or ten hours, especially if a little excess of methylic

iodide be present, most of the ether will become converted into the β-compound.

The boiling point of the ether prepared as above is lower than that I previously gave, probably on account of its greater freedom from the β-compound, viz., 275—276°. Its specific gravity at 15° is 1·1404, and at 30° 1·1277 compared with water at the same temperatures.

A determination of its magnetic rotary power gave for the yellow ray 2·334, water being taken as 1.*

With concentrated sulphuric acid it yields a soluble acid.

β-Methylorthoxyphenylacrylic Acid.

This acid, as usually prepared from the hydride of methylsalicyl, acetic anhydride, and sodic acetate, is of a pale-yellow colour, and this is only slowly removed by crystallisation from alcohol. If, however, coal-tar naphtha be employed instead of alcohol, it is easily obtained perfectly white, and apparently slightly fluorescent. The acid thus purified melts at 178—179°. The crystals of this body have been measured; they belong to the oblique system. For their description, see the end of this paper.

Methylic β-Methylorthoxyphenylacrylate.

This compound was prepared from the above acid by converting it into its chloride with phosphoric chloride, and then adding the chloride by degrees to methyl alcohol. The product was mixed with water to remove the excess of methyl alcohol, &c. The somewhat thick oily ether was then collected, diluted with ordinary ether, and left to dry over potassium carbonate. It was then distilled; as soon as most of the ordinary ether had been driven over, the thermometer rapidly rose and became stationary at 293°, at which temperature nearly all of the new product came over. It gave on analysis the following numbers:—

0·0975 of substance gave 0·2463 of CO_2, and 0·0568 of OH_2.

	Theory for $C_{11}H_{12}O_3$.	Experiment.
Carbon	68·75	68·89
Hydrogen	6·25	6·47

Methylic β-methylorthoxyphenylacrylate is a thick, highly refracting oil. Its specific gravity at 15° is 1·1486; at 30°, 1·1362, compared with water at same temperatures.

* Test observations were made at the same time with water and carbon bisulphide, and gave results very nearly identical with those obtained by Becquerel. (*Ann. Chem. Phys.*, 1877, **12**, 22.)

Determinations of its magnetic rotary power for the yellow ray gave 2·389. The vapour of this ether, as also of its isomeride, when inhaled, causes headache.

With nitric acid it forms an orange-coloured, semi-solid, amorphous mass. Concentrated sulphuric acid yields with it a soluble acid.

α-Ethylorthoxyphenylacrylic Acid.

14½ grams of coumarin were dissolved in a solution of pure sodic hydrate containing 8 grams of alkali. The resulting product was then boiled down to a small bulk, diluted with alcohol, and 32 grams of ethylic iodide added. This mixture was placed in a soda-water bottle, and heated to 100° for four or five hours. Most of the alcohol was then distilled off, and the residue mixed with ether and water, the latter to remove the sodic iodide. The ethereal solution was then agitated with dilute caustic alkali, and after being separated, placed over potassium carbonate to dry. This contains most of the product of the reaction, viz., ethylic α-ethylorthoxyphenylacrylate, and is separated from the ether by distillation. The dilute alkali with which the ethereal solution of this ether was washed, yielded when acidified an oil, which solidified after some time. This weighed about 3 grams, and consisted of the new acid. It was crystallised from petroleum spirit, then from alcohol, and analysed. The following numbers were obtained:—

0·1683 of substance gave 0·4242 of CO_2, and 0·0942 of OH_2.

These numbers agree with those required by the formula—

$$C_{11}H_{12}O_3 = C_6H_4(OC_2H_5)—CH{=}CH—COOH.$$

	Theory.	Experiment.
Carbon	68·75	68·74
Hydrogen	6·25	6·22

This substance is therefore *ethylorthoxyphenylacrylic acid*, and from its properties and mode of preparation is evidently the α-acid. Its formation resulted from the imperfect action of the ethyl iodide on the sodium compound of the coumarin, one atom of the metal only being attacked. Small quantities of the α-acids are usually found associated with their ethers when preparing them from the coumarins from this same cause. Ethylorthoxyphenylacrylic acid can also be easily obtained from its ether by decomposing it with alcoholic potash.

α-ethylorthoxyphenylacrylic acid crystallises very beautifully, and similarly to its methylic homologue, the crystals refracting light very strongly. It melts at 103—104°. It is very soluble in alcohol, and this solvent when supersaturated with it, will sometimes remain perfectly clear for days, but if a single crystal of the acid be placed in it,

it grows very rapidly and beautifully. It is easily soluble in boiling carbon disulphide, from which it crystallises out very readily on cooling; in hot petroleum spirit it is moderately soluble.

When exposed to the action of heat it changes into its isomeride the β-acid.

Ethylic α-Ethylorthoxyphenylacrylate.

The preparation of this ether has already been given. It boils at about 290—291°, but towards the end of the distillation the temperature gradually rises, apparently from the formation of a small quantity of the β-ether during the operation. On analysis it gave the following numbers:—

0·1328 of substance gave 0·3443 of CO_2, and 0·0884 of OH_2.

These numbers agree with those required by the formula—

$$C_{13}H_{16}O_3 = C_6H_4(OC_2H_5)—CH=CH—CO(OC_2H_5).$$

	Theory.	Experiment.
Carbon	70·9	70·78
Hydrogen	7·2	7·39

Ethylic ethylorthoxyphenylacrylate is a colourless, transparent, highly refracting oil. Its specific gravity

at 15° is 1·084
at 30 is 1·074

compared with water at same temperatures.

Determinations of its magnetic rotary power gave for the sodium line 2·175, water = 1.

β-Ethylorthoxyphenylacrylic Acid.

This acid was prepared by heating a mixture of hydride of ethyl salicyl, acetic anhydride, and sodic acetate in sealed tubes to 160—170°. The product on cooling solidified to a crystalline mass, and on opening the tubes carbonic anhydride escaped. The contents of the tubes were mixed with water and distilled until oily matter ceased to come over. On cooling, the crude oily acid left in the retort solidified to a crystalline mass, and the aqueous fluid covering it became filled with white needles. After filtering off the solution of sodic acetate, the crude acid was dissolved in a solution of sodic carbonate, and all the neutral oils separated. It was then precipitated with hydrochloric acid, washed, dried, and crystallised from alcohol two or three times.

On analysis it gave the following numbers:—

0·2134 of substance gave 0·5396 of CO_2, and 0·1211 of OH_2.

	Theory for $C_{11}H_{12}O_3$.	Experiment.
Carbon	68·74	68·96
Hydrogen	6·25	6·3

β-ethylorthoxyphenylacrylic differs considerably from the α-isomeride. It melts at 135°. It is easily soluble in boiling alcohol, and comes down from it in small prisms as it cools; it is not very soluble in cold alcohol. Boiling benzene dissolves it easily, depositing most of it on cooling in white needles, more colourless than when alcohol is employed. It bears a considerable resemblance to its homologue, β-methylorthoxyphenylacrylic acid.

Ethylic β-Ethylorthoxyphenylacrylate.

This ether is prepared from the chloride of the above by acting on it with ethylic alcohol. It boils at 302—304°, and is a thick, highly refracting liquid. A determination of its specific gravity was made, and gave a number nearly identical with that of the α-compound, but a little doubt exists as to the purity of the product used in this determination. A specimen obtained by boiling the α-ether for some time and fractioning it, gave specific gravity 1·090 at 15°.

REFRACTIVE INDICES OF METHYLIC α- and β-METHYL-ORTHOXYPHENYLACRYLATE AND ETHYLIC α-ETHYLORTHOXYPHENYLACRYLATE.

I am indebted to the kindness of Dr. J. H. Gladstone for these determinations, and the annexed account of them.

"The following are the refractive indices of the α- and β-methylorthoxyphenylacrylate of methyl, and of the analogous ethyl compound:—

Compound.	Temp.	μ_A.	μ_D.	μ_H.
α-Methylorthoxyphenylacrylate of methyl.	8·0°	1·5577	1·5727	1·6428
α- do. do.	10·5	1·5572	1·5718	1·6421
β- do. do.	9·5	1·5722	1·5912	1·6860?
β- do. do.	10 0	1·5722	1·5905	1·6818?
α-Ethylorthoxyphenylacrylate of ethyl ...	10·0	1·5438	1·5579	1·6298

"There is a little doubt as to the precise refraction of H in the β-methyl compound, as the spectrum was absorbed at about this point.

"The following may be taken as the refractive equivalents for A and for H, being the mean of the observations:—

Compound.	A.	H.	Dispersion equivalent.
α-Methylorthoxyphenylacrylate of methyl ...	93·42	107·58	14·16
β- do. do.	95·10	113·66	18·56
α-Ethylorthoxyphenylacrylate of ethyl	109·76	127·11	17·35

"These figures present two points of remarkable interest. 1st. The refraction equivalent is exceedingly high; calculated for the usual values of C, H, and O, the methyl compound would give us only the refractive equivalent of 73·3 for A; even if all the carbon had the same value as in the ordinary phenyl compounds, it would not give so large a figure; and we must conclude that a portion of it is in the most refractive condition known. The body most analogous to it in this respect is the hydride of cinnamyl. 2nd. The two isomeric modifications of the methyl compound, though they do not differ widely in the refraction equivalent for A, are extremely different in dispersion, the increase for the β-compound being about 30 per cent. This is the only instance with which I am acquainted of two isomeric bodies differing largely in dispersion, but not in their initial refraction.

"The optical properties of the ethyl compound resemble those of its methyl homologue, but are more nearly in accordance with the β- than with the α-modification, the usual difference of refraction-equivalent for $2(CH_2)$ being 15·2."

Action of Nascent Hydrogen on α- and β-Methylorthoxyphenylacrylic Acids.

Separate solutions of the sodic salts of these acids were left in contact with sodium-amalgam for a few hours. On being acidified with hydrochloric acid, they both gave crystalline products apparently identical. They were washed, converted into baric salts, which were purified by recrystallisation, dissolved in water, and again precipitated by hydrochloric acid, and lastly crystallised from petroleum spirit. On analysis they gave the following numbers:—

I. 0·1897 of substance prepared from β-acid gave 0·4636 of CO_2, and 0·1144 of OH_2.

II. 0·1252 of substance prepared from α-acid gave 0·3064 of CO_2, and 0·0747 of OH_2.

These numbers give percentages agreeing with those required for the formula—

$$C_{10}H_{12}O_3 = C_6H_4(OCH_3)—CH_2—CH_2—COOH.$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	66·66	66·65	66·74
Hydrogen	6·66	6·70	6·63

It may be called *dihydromethylorthoxyphenyacrylic*, *methylmellilotic*, or better, *methylorthoxyphenylpropionic acid.*

The preparations made with the α- and β-acids were identical.

This acid melts at 92°; if not purified by conversion into the baric salt, it generally melts at about 87°. It is very soluble in boiling alcohol, and crystallises out from it on cooling in transparent crystals, which when viewed with a lens, are not unlike sodic sulphate. It is only moderately soluble in petroleum spirit, and crystallises from it in small brilliant prisms. Boiling water also dissolves it to a small extent, and deposits it on cooling in lance-like leaves, but if made to crystallise quickly, as oblique plates, which when viewed under the microscope with polarised light, exhibit most beautifully varied and brilliant colours.

Baric Methylorthoxyphenylpropionate.—The acid, when boiled with a solution of baric hydrate dissolves, and after treating the solution with carbonic acid, boiling, and filtering off the baric carbonate formed, a solution of this salt is obtained, which, when concentrated, deposits it in satiny needles, moderately soluble in cold, easily so in hot water.

A solution of this salt gives with silver nitrate an amorphous white precipitate soluble in boiling water, and deposited from it on cooling as a white apparently crystalline powder. With ferric chloride it gives a very pale brown precipitate, which when rubbed contracts to a semi-solid brown mass. With lead acetate it forms a product like lead plaster.

Action of Nitric Acid (sp. gr. 1·5) on α- and β-Methylorthoxyphenylacrylic Acids.

These acids are vigorously acted upon by nitric acid (sp. gr. 1·5), and therefore require to be added to it very slowly, and in small quantities at a time. The nitric acid should also be kept cooled. On pouring the product into water, a drab-coloured substance separates. This was collected, washed, pressed, and crystallised from alcohol several times. The α- and β-acids both yield the same product, but the β gives it in the purest condition, and in largest quantity, and therefore it requires to be recrystallised less frequently. The substance gave the following numbers on analysis:—

I. 0·1474 of substance gave 0·2412 of CO_2, and 0·0420 of OH_2.

II. 0·0953 of substance gave 0·1549 of CO_2, and 0·0262 of OH_2.

III. 0·1080 of substance gave 0·1763 of CO_2, and 0·0315 of OH_2.
IV. 0·2192 of substance gave 20 c.c. of nitrogen at 12·5° and 731·7 mm.

These numbers give percentages agreeing with the formula—

$$C_{10}H_8(NO_2)_2O_3.$$

	Theory.	Experiment. I.	II.	III.	IV.
Carbon	44·77	44·62	44·32	44 52	—
Hydrogen	2·98	3·16	3·05	3·24	—
Nitrogen.....	10·44	—	—	—	10·55

The product used in Nos. I, III, and IV was prepared from the β-acid, the other from the α.

This substance is therefore *methylorthoxydinitrophenylacrylic acid*. It melts at about 192—193°, but decomposes a little before reaching that point. It is moderately soluble in boiling alcohol, and crystallises out from it on cooling in bright orange-brown clusters of needles. Cold alcohol dissolves it only to a small extent; this is also the case with boiling benzene. It is nearly insoluble in chloroform.

Aqueous potassic hydrate and also ammonia dissolve it, forming a bright yellow coloured solution, from which hydrochloric acid precipitates it as a light drab powder. Alcoholic potassic hydrate also dissolves it, forming a beautiful cerise-coloured solution.

Action of Bromine on α- and β-Methylorthoxyphenylacrylic Acids.

Weighed quantities of these acids were placed with a vessel of bromine under a bell-jar in the dark. The bromine vapour was rapidly absorbed, and hydrobromic acid formed. After about twelve hours' exposure, the products were removed and placed under another bell-jar with potassic hydrate for about two days until free from excess of bromine. On weighing the products, it was found that they had both absorbed bromine in the same proportion, viz., 3 atoms. The products were crystallised from benzene, and on analysis gave the following numbers:—

I. 0·1337 of substance gave 0·1406 of CO_2, and 0·0279 of OH_2.
II. 0·1716 of substance gave 0·1790 of CO_2, and 0·0340 of OH_2.

No. I was made from the α-, and No. II from the β-acid.

From these numbers it will be seen that this substance has the formula—

$$C_{10}H_9Br_3O_3.$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	28·75	28·68	28·45
Hydrogen	2·13	2·31	2·20

The identity of the products made from the α- and β-acids was shown by determinations of their solubilities in chloroform, which gave the following results:—

Substance prepared from α-acid 0·413 in 100 of chloroform.
" " β- " 0·43 " "

Their behaviour with reagents was also identical.

The formation of this substance may be represented thus—

$$C_{10}H_{10}O_3 + 4Br = C_{10}H_9Br_3O_3 + HBr;$$

and as will be seen further on, its constitution may be regarded as—

$$C_6H_3Br(OCH_3)—CHBr—CHBr—COOH.$$

It is proposed to call it *methylorthoxybromophenyldibromopropionic acid*. When heated, this substance melts at about 185—188° with decomposition. It is moderately soluble in hot benzene, and crystallises from it on cooling in white nodular masses. It is very little soluble in this hydrocarbon when cold. It is very soluble in ether; alcohol appears to decompose it.

Aqueous ammonia dissolves this substance, but the solution soon becomes milky, especially if heated, and on standing a crystalline product separates out. Dilute sodic carbonate or potassic hydrate also dissolves it, but the solution quickly becomes milky, and, if warmed, a heavy oil separates. A strong solution of caustic alkali, however, does not appear to decompose it.

Boiled with a solution of sodic acetate it gives off carbonic acid with separation of an oil. This oil is carried over very slowly by aqueous vapour. It gave the following numbers on analysis:—

I. 0·1747 of substance gave 0·2290 of CO_2, and 0·0420 of OH_2.
II. 0·1780 of substance gave 0·2328 of CO_2, and 0·0415 of OH_2.

These numbers show the substance to have the formula $C_9H_8Br_2O$, which represents *dibromorthovinyl-anisoïl*.

	Theory.	Experiment. I.	Experiment. II.
Carbon	35·06	35·75	35·66
Hydrogen	2·59	2·67	2·59

It is a pale yellow oil, quite viscid when cold; its formation may be represented thus:—

$$C_6H_3Br(OCH)—C_2H_2Br_2—COOH = C_6H_3Br(OCH_3)—C_2H_2Br + CO_2 + HBr.$$

Action of a Strong Solution of Potassic Hydrate on Methylorthoxybromophenyldibromopropionic Acid.

It has just been stated that a dilute solution of potassic hydrate decomposes methylorthoxybromophenyldibromopropionic acid with separation of an oil. But if a concentrated solution of potassic hydrate (about 50 per cent. was used) be rubbed with it in a mortar, it evidently combines with it, but does not seem to undergo decomposition, apparently because it does not enter into solution. This mixture was heated to 100° for some time, when potassic bromide formed in quantity. It was then dissolved in water, and found to contain a small quantity of an oily body. This was removed, and the solution acidified, when a crystalline acid, still containing bromine, separated. This acid was collected, washed, and boiled with dilute potassic hydrate, and again precipitated with hydrochloric acid. As this process had not removed the bromine from the new acid, it was washed, dried, and dissolved in boiling benzene, from which it separated on cooling in short white needles, which gave the following numbers on analysis:—

0·1650 of substance gave 0·2856 of CO_2, and 0·0426 of OH_2.

These numbers give percentages agreeing with those required by the formula—

$$C_{10}H_7BrO_3.$$

	Theory.	Experiment.
Carbon	47·06	47·2
Hydrogen	2·74	2·86

This substance is *methylorthoxybromophenylpropiolic acid.* The formation indicates that one of the bromine-atoms in the tribromomethylorthoxyphenylpropionic acid is in the benzene group, as it cannot be removed by boiling alkali. The decomposition may be written thus:—

$$C_6H_3Br(OCH_3)—CHBr—CHBr—COOH = 2HBr +$$

Methylorthoxybromphenyldibromopropionic acid.

$$C_6H_3Br(OCH_3)—C\equiv C—COOH$$

Methylorthoxybromophenylpropiolic acid.

This acid melts at about 168° with decomposition, becoming yellow. It is moderately soluble in hot, but sparingly in cold benzene. It crystallises from this solvent in short white needles.

Action of Bromine in a Limited Quantity on α- and β-Methylorthoxyphenylacrylic Acids.

I. *Action on α-Methylorthoxyphenylacrylic Acid.*

A weighed quantity of this acid was dissolved in carbon disulphide, and the solution thus obtained when cold was treated by degrees with a 10 per cent. solution of bromine also in carbon disulphide, sufficient being added to form a dibromo-addition product. The bromine quickly combined at first, but more slowly as the last portions were added, a small quantity only of hydrobromic acid being formed. On standing for some time, the sides of the vessel became coated with small brilliant crystals. These were collected, washed with carbon disulphide, and dried in the air, and then *in vacuo*. They gave on analysis the following numbers:—

I. 0·1180 of substance gave 0·1534 of CO_2, and 0·0286 of OH_2.
II. 0·1405 of substance gave 0·1823 of CO_2, and 0·0386 of OH_2.

These numbers give percentages agreeing with the formula—

$$C_{10}H_{10}Br_2O_3.$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	35·5	35·44	35·38
Hydrogen	2·95	2·69	3·06

The acid is therefore *α-methylorthoxyphenyldibromopropionic acid.* It decomposes if heated for any length of time at 100°. If quickly heated it melts at about 156°, but it does not give any definite fusing point owing to its decomposition. It is moderately soluble in chloroform, and separates from it in flat transparent prisms. Chloroform may be used instead of carbon disulphide in its preparation. It dissolves easily in alcohol with decomposition. The changes it undergoes with various reagents will be found further on.

When exposed to the action of the vapour of bromine for about 24 hours, it gives a product which crystallises from benzene in brilliant apparently oblique crystals, giving on analysis the following numbers:—

0·1006 of substance gave 0·0886 of CO_2, and 0·0174 of OH_2.

These give percentages agreeing with the formula—

$$C_{10}H_8Br_4O_3.$$

	Theory.	Experiment.
Carbon	24·19	23·94
Hydrogen	1·61	1·92

It may be called *methylorthoxydibromophenyldibromopropionic* acid. It melts at about 200—202°.

II. *Action on β-Methylorthoxyphenylacrylic Acid.*

A weighed quantity of this acid was dissolved in chloroform, of which it required a considerable volume, being difficultly soluble, the calculated quantity of bromine also in chloroform, to form a dibromo-addition body, was then gradually added. The combination took place as in the case of the α-acid, but not so rapidly. After standing for some hours most of the chloroform was distilled off, and the remaining solution on cooling gradually deposited crystals. These were collected and recrystallised from chloroform, and were thus obtained perfectly white. This body gave on analysis the following numbers :—

I. 0·1672 of substance gave 0·2191 of CO_2 and 0·0468 of OH_2.
II. 0·1170 of substance gave 0·1524 of CO_2 and 0·0318 of OH_2.

This substance has therefore the same formula as the last, viz. :—

$C_{10}H_{10}Br_2O_3$.

	Theory.	Experiment. I.	Experiment. II.
Carbon	35·5	35·73	35·51
Hydrogen	2·95	3·11	3·01

It suffers decomposition at 100° slowly. Combustion I was made with a product dried at 100° for some time ; II, *in vacuo*. I was at first inclined to regard this as identical with the product obtained from the α-acid, but its fusing point, although indefinite from decomposition, appeared to be somewhat higher. I therefore made determinations of the solubility of the two products, with the following results :—

	α.	β.
Solubility in 100 vols. of CS_2	0·074	0·4
„ „ $CHCl_3$ ..	1·927	6·64

These show that the products are isomeric, and not identical; so they have been called α- and *β-methylorthoxphenyldibromopropionic acids*. The β-compound generally forms rather larger and more brilliant crystals than the α. It is rather remarkable that although obtained from the least soluble acid it should be the more soluble compound of the two.

α- and β-methylorthoxyphenyldibromopropionic acids possess the following properties in common. They are easily soluble in ether, freely in alcohol, but with decomposition, the solution becoming acid,

and moderately in glacial acetic acid. On the addition of aqueous silver nitrate to these solutions, a copious precipitate of silver bromide forms. When shaken with cold water the liquid becomes milky, and if heated to boiling, globules of an oil condense with the steam; the solution also becomes strongly acid. With dilute potassic hydrate, ammonia, sodic carbonate, or sodic acetate, these compounds decompose, with formation of an oil; this decomposition is accelerated by heat. The oil has an odour like that of orthovinylanisoïl, and is probably its bromine derivative.

Action of a Strong Solution of Potassic Hydrate on α- and β-Methylorthoxyphenyldibromopropionic Acids.

I. A quantity of the α-methylorthoxyphenyldibromopropionic acid was rubbed into a paste with a strong solution of potassic hydrate (about 50 per cent.), and then stirred from time to time. After being in contact with the alkali a few hours, the mixture was acidified with dilute hydrochloric acid, and the white crystalline product which resulted collected, washed, and crystallised from boiling water. In this manner it was obtained in glistening needles.

It was then further purified by recrystallisation from carbon disulphide. A very small quantity of oily product was produced in this reaction. The substance gave the following numbers on analysis:—

0·1130 of substance gave 0·1931 of CO_2, and 0·0379 of OH_2.

These give percentages required by the formula—

$C_{10}H_9BrO_3$.

	Theory.	Experiment.
Carbon.....	46·69	46·6
Hydrogen	3·5	3·7

It is therefore *methylorthoxyphenylbromacrylic acid.*

II. Some of the β-methylorthoxyphenyldibromopropionic acid was treated in the same manner as the α with caustic alkali. It behaved in a similar way, and the product gave on analysis the following numbers:—

I. 0·1561 of substance gave 0·2677 of CO_2, and 0·0525 of OH_2.
II. 0·2485 of substance gave 0·1820 of AgBr,

which yield percentages analogous to the above, viz.:—

	Theory.	Experiment.
Carbon.....	46·69	46·75
Hydrogen	3·5	3·5
Bromine	31·12	31·16

The products obtained from the two dibromo-acids both melt at the same temperature, and from a determination of their solubility in carbon disulphide they are evidently identical, 100 vols. of CS_2 at 14° dissolving 0·31 of the α- and 0·33 of the β-acid. These determinations were made on only small quantities, otherwise they would probably have been still more accordant. The formation of this acid from these two dibromo-acids is evidently due to removal of hydrobromic acid, thus:—

$$C_{10}H_{10}Br_2O_3 = HBr + C_{10}H_9BrO_3.$$

Alcoholic potassic hydrate may be employed in the preparation of this acid instead of aqueous, but the product is not generally so pure.

Methylorthoxyphenylbromacrylic acid melts at 169·5—171°, and on cooling solidifies to a radiating crystalline mass. The vapour it gives off when heated is very irritating. It can be distilled apparently without decomposition. It is moderately soluble in boiling carbon disulphide, and crystallises out from it on cooling in small brilliant prisms. It is difficultly soluble in petroleum spirit, but easily so in alcohol. Boiling water dissolves it to a small extent only, but in cold water it is nearly insoluble. In aqueous sodic acetate it is easily soluble, but is precipitated on the addition of hydrochloric acid.

Dilute aqueous potassic hydrate dissolves it freely, but on the addition of a concentrated solution the potassic salt separates out in a crystalline condition. The solution in aqueous ammonia when evaporated *in vacuo* leaves a crystalline salt soluble in water.

Nitric acid 1·5 sp. gr. acts vigorously on this acid, dissolving it, and on the addition of water a light drab-coloured precipitate forms, which conglomerates, but afterwards becomes pulverulent. On crystallising this from alcohol, it is obtained in small yellow needles. It is probably a dinitro-compound of the bromo-acid, as it gives with alcoholic potassic hydrate a beautiful cerise-coloured solution.

Decomposition of Methylorthoxyphenylbromacrylic Acid by Alkalies.

On boiling a solution of methylorthoxyphenylbromacrylic acid in a dilute solution of potassic hydrate, potassic bromide is formed, and the solution when acidified with hydrochloric acid deposits a crystalline acid; as this, however, is rather soluble in hot water, it takes some hours before it ceases to separate out. The acid obtained in this manner, after being washed with cold water, was dissolved in boiling water. The resulting solution on cooling became a mass of fine white needles, perfectly filling the liquid, so that the mother-liquor could not be poured off freely; when stirred, however, it became quite fluid, and the crystals could then be easily separated by a filter.

The mother-liquors when concentrated yielded a further quantity of this product. It was then crystallised from benzene, and on analysis gave the following numbers:—

I. 0·1134 of substance gave 0·2848 of CO_2, and 0·0516 of OH_2.
II. 0·1131 of substance gave 0·2827 of CO_2, and 0·0513 of OH_2.

These numbers lead to the formula $C_{10}H_8O_3$.

	Theory.	Experiment. I.	Experiment. II.
Carbon	68·18	68·4	68·17
Hydrogen.....	4·54	4·97	5·03

It is therefore *methylorthoxyphenylpropiolic acid*, its formation being due to the separation of hydrobromic acid from methylorthoxyphenylbromacrylic acid, thus:—

$$C_6H_4(OCH_3)—C_2HBr—COOH = C_6H_4(OCH_3)—C_2—COOH + HBr.$$

This acid is moderately soluble in benzene, freely in alcohol and ether, but difficultly in carbon disulphide, the boiling solution in this solvent depositing it on cooling in brilliant needles. It melts at about 124—126°, with decomposition.

With strong nitric acid it forms a dark greenish indigo-coloured fluid, which soon changes to a reddish-buff colour. The addition of water then causes the separation of yellowish-brown flocks. This product does not give any coloured reaction when heated with an alkali and grape-sugar.

Methylorthoxyphenylpropiolic acid dissolves easily in dilute potassic hydrate. A strong solution added to this causes the potassium salt to separate in minute needles. Sodic hydrate acts in a similar manner, but the salt formed is only a confused crystalline precipitate.

Ammonia dissolves this acid freely, but the solution when evaporated is decomposed.

Silver nitrate gives with a solution of the ammonia salt a copious somewhat curdy white precipitate.

Action of Bromine on the Methylic α- and β-Methylorthoxyphenylacrylates.

As the dibromo-derivatives of the α- and β-acid were found to be isomeric, it was thought desirable to see if the ethers would yield analogous products.

I. *Action of Bromine on Methylic-β-Methylorthoxyphenylacrylate.*—The following is an account of one out of several operations of this kind, and is taken as it is roughly comparable with an analogous one made with the α-compound given further on.

3 grams of the β-compound were mixed with two or three times their bulk of carbon disulphide, and sufficient of a 10 per cent. solution of bromine in carbon disulphide to form a dibromide with the ether, gradually poured in. The bromine readily combined until the last quantities were added, when the fluid remained slightly coloured for some time; very little hydrobromic acid was formed. It was then placed in the dark and allowed to evaporate spontaneously, when crystals began to form after a time, but not until nearly all the carbon disulphide had disappeared. The residue then consisted of a mixture of crystals and a thick mother-liquor. The crystals were separated by washing with a little carbon disulphide, and weighed about 1·7 grams.

This substance was purified by recrystallisation once or twice from carbon disulphide, and gave on analysis the following numbers:—

0·1844 of substance gave 0·2538 of CO_2, and 0·0586 of OH_2.

These give percentages required by the formula—

$$C_{11}H_{12}Br_2O_3.$$

	Theory.	Experiment.
Carbon	37·42	37·53
Hydrogen	3·41	3·53

This compound melts at 125°. Its other properties will be referred to further on.

The thick mother-liquors formed at the same time as these crystals, when left exposed to the air for some days, and until perfectly free from carbon disulphide, solidify to a crystalline mass. This was purified by two or three crystallisations from petroleum spirit (b. p. 70—100°). It was gradually deposited from this solvent in hard groups of crystals. The weight of the product obtained in this operation after one crystallisation was 3·5 grams, so that it is the principal product of the reaction.

It gave the following numbers on analysis:—

I. 0·1215 of substance gave 0·1658 of CO_2, and 0·386 of OH_2.
II. 0·2438 of substance gave 0·2598 of AgBr.

This substance has the same composition as the one just described.

		Experiment.	
Theory for $C_{11}H_{12}Br_2O_3$.		I.	II.
Carbon	37·42	37·21	—
Hydrogen	3·41	3·5	—
Bromine	45·45	—	45·35

It is, however, isomeric, its melting point being only 68°. I propose

to call it methylic β-methylorthoxyphenyldibromopropionate. It is exceedingly soluble in carbon disulphide and easily soluble in alcohol.

When treated with cold alcoholic potash it soon dissolves, potassic bromide is deposited, and the solution contains methylorthoxyphenylbromacrylic acid, in combination with the alkali. This, when separated and purified, was found to melt at 169°, and when boiled with a solution of potassic hydrate to decompose into methylorthoxyphenylpropiolate and potassic bromide, so that it is evidently identical with the acid obtained from methylorthoxyphenyldibromopropionic acid already described.

II. *Action of Bromine on Methylic α-Methylorthoxyphenylacrylate.*—3 grams of the α-compound were treated with bromine in exactly the same manner as the β-compound; and the reaction appeared to proceed in the same way, very little hydrobromic acid being formed. The mixture was placed in the dark, and allowed to evaporate spontaneously. In this case, however, crystals rapidly began to form on the sides of the vessel. When the carbon disulphide was mostly evaporated these were collected, washed rapidly with carbon disulphide, dried, and weighed. They weighed 3·5 grams. The mother-liquor on evaporation yielded a second crop of the same crystals, which, however, were unfortunately not weighed.

This crystalline product was purified by recrystallisation from carbon disulphide, and on analysis gave the following numbers :—

I. 0·1749 of substance gave 0·2400 CO_2, and 0·0582 of OH_2.
II. 0·2710 of substance gave 0·2900 of AgBr.

This substance corresponds in composition with the two foregoing ones:—

		Experiment.	
Theory for $C_{11}H_{12}Br_2O_3$.		I.	II.
Carbon	37·42	37·42	—
Hydrogen.....	3·41	3·69	—
Bromine	45·45	—	45·53

This body, which I propose to call *methylic α-methylorthoxyphenyldibromopropionate*, melts at 125°; it is evidently the chief product of the reaction, and is identical with the substance obtained in comparatively small quantities with the β-ether, fusing at the same temperature. A comparison of the solubilities in carbon disulphide of the products from these two ethers was made, and gave the following numbers :—

Bromine-derivative from α-compound, 3·38, in 100 vols. CS_2.
„ „ β- „ 3·46 „ „

This body forms crystals sometimes like calcspar, at other times in

more complicated forms; they are very transparent. It may be crystallised from alcohol, in which it is easily soluble when boiling, but only moderately when cold; a certain amount, however, undergoes decomposition, the solution becoming acid even in a short time, and strongly so after a few minutes' boiling. It is moderately soluble in boiling petroleum spirit.

Alcoholic potash dissolves the substance slowly, potassic bromide forming. The result of this reaction is, as in the case of the β-bromine derivative, ordinary methylorthoxyphenylbromacrylic acid, fusing at 169°.

The mother-liquors from the preparation of this α-dibromo-compound were found to contain some of the β-dibromo-compound, fusing at 68°, over 0·7 gram being obtained.

We therefore see the curious result of these experiments to be that the α-ether produces as its chief product the dibromo-derivative melting at 125°, with a small quantity of the dibromo-compound melting at 68°. The β-ether produces as its chief product the dibromo-compound melting at 68°, with a considerable quantity (about 30 per cent. of the theoretical yield) of the dibromo-compound melting at 125°.

In considering these results, it must be borne in mind that the amount of the dibromo-compound fusing at 68° produced from the α-ether is greater than should be produced were the ether perfectly pure, because the α-ether in its preparation, having to be distilled, becomes partially changed into the β-ether, which would principally yield this bromo-body; but these remarks do not in any way apply to the formation of the dibromo-compound melting at 125°, from the β-ether, as that was perfectly free from the α; it must therefore be regarded as a true product of the reaction. This behaviour is somewhat analogous to that of the two hydrobenzoïns when treated with phosphoric chloride, the iso-compound giving a chloride only, fusing at 192°, the ordinary hydrobenzoïn giving this, and also one fusing at 94°.

Action of Bromine on Ethylic α- and β-Ethylorthoxyphenylacrylates.

These ethers, when treated in the same manner as the corresponding methylic compounds, act very similarly. The α-product, when the carbon disulphide has evaporated, gives a crystalline product mixed with a honey-like oil, which was removed by petroleum spirit. The product obtained from the β-ether was at first only an oil, but on keeping it exposed to the air for a number of days crystals separated out. The quantity obtained was, however, only small, the principal product being an oil, which could not be obtained in a fit condition for analysis.

The crystalline products obtained from these ethers were recrystal-

lised from petroleum, and were found to fuse at the same temperature, so that they are evidently identical. A specimen prepared from the α-ether gave on analysis the following numbers:—

0·1363 of substance gave 0·2031 of CO_2, and 0·0517 of OH_2.

These give percentages agreeing with the formula—

$$C_{13}H_{16}Br_2O_3 = C_6H_4(OC_2H_5)—CHBr—CHBr—CO(OC_2H_5).$$

	Theory.	Experiment.
Carbon	41·05	40·64
Hydrogen	4·21	4·2

This body may be called *ethylic ethylorthoxyphenyldibromopropionate.* It melts at 78°. It is rather easily soluble in hot petroleum spirit, and crystallises from it in small transparent prisms, sometimes having the appearance of hexagonal plates.

Action of Alcoholic Potassic Hydrate on Ethylorthoxyphenyldibromopropionate.

This substance, when mixed with cold alcoholic potassic hydrate, gives potassic bromide, and the solution is found to contain a new acid, which was separated by diluting with water and acidifying with hydrochloric acid; it was then collected and washed.

This was crystallised from boiling water in which it is difficultly soluble, and then from carbon disulphide. It gave on analysis the following numbers:—

0·1130 of substance gave 0·2016 of CO_2, and 0·0438 of OH_2.

From the percentages these numbers give it will be seen that this substance has the formula—

$$C_{11}H_{11}BrO_3 = C_6H_4.(OC_2H_5)—C_2HBr—COOH,$$

and is therefore *ethylorthoxylphenylbromacrylic acid.*

	Theory.	Experiment.
Carbon.....	48·7	48·65
Hydrogen	4·05	4·3

This substance melts at 164°, and may be distilled without decomposition. It crystallises apparently in flat square prisms, the product when pressed having a satiny aspect. It is rather difficultly soluble in carbon disulphide, easily so in chloroform and in alcohol.

The oily product obtained by the action of bromine on β-ethylic ethylorthoxyphenyl acrylate, appears to yield this acid when treated with alcoholic potassic hydrate.

When this acid is boiled with potassic hydrate, all the bromine is removed from it, and a product, which is evidently ethylorthoxyphenylpropiolic acid, is obtained. It crystallises from water very similarly to the methylic derivative already described, and with nitric acid it also gives the same coloured reaction.

α-Methylorthoxyphenylacrylic Acid and Hydriodic Acid (fuming).

The acids when left in contact for some time unite, and the product, when treated with a solution of sodic carbonate, decomposes, with the formation of orthovinylanisoïl. It appeared to be exactly the same as that obtained in a similar manner from the β-acid. This was confirmed by a determination of its density.

	Product from α-acid.	From β-acid.
Sp. gr. at 15°	1·0093	1·0095
„ 30	1·001	1·000

α- and β-Methylorthoxylphenylacrylic Acid and Hypochlorous Acid.

On passing chlorine into a solution of these acids in sodic carbonate, they behave exactly alike. The solutions become turbid, and an oil gradually accumulates, and is the principal product of the reaction. It was purified and analysed, but was not a definite body, the numbers seeming to show that it was composed of mono- and dichlor-orthovinylanisoïl. A small quantity of a gummy acid was obtained from the aqueous solution, but in too small a quantity to admit of examination.

Products Derived from Propionic Coumarin.

Methylic-α-Methylorthoxyphenylcrotonate.

As I have previously shown, propionic coumarin behaves like the ordinary one with caustic alkalies, forming saline compounds, which when treated with acids decompose with regeneration of the propionic coumarin. A quantity of the sodic compound of this coumarin was treated with methyl iodide in order to obtain a compound corresponding to α-methylorthoxyphenylacrylic acid. The proportions used were 10 of propionic coumarin, 5 of pure sodic hydrate, and 18 of methylic iodide. The propionic coumarin was first boiled with water and the sodic hydrate until dissolved, the resulting solution concentrated, mixed with alcohol and the methylic iodide, and then heated to 100° in a soda-water bottle securely corked for three or four hours. The alcohol was distilled off, water and ether added to facilitate the separation of the sodic iodide from the oily product which had been formed. The ethereal solution was then agitated with a solution of

sodic carbonate, which removes a small quantity of the new acid held in solution by the ether. It was then separated, dried over potassic carbonate, and distilled.

After the ether had passed over, the temperature rapidly increased until it reached 274—275°, when it remained constant for some time; it then rapidly rose, owing to the presence of some unchanged propionic coumarin. This is always present to some extent, even in the latter part of the fraction boiling within the above limits; and after a number of combustions had been made, it was found that only the early portions of the distillate were sufficiently pure to give good numbers, a very small quantity of propionic coumarin making a considerable difference in the percentage composition. The following are some of the results obtained on its analysis:—

I. 0·1196 of substance gave 0·3060 of CO_2, and 0·0726 of OH_2.
II. 0·1165 of substance gave 0·2968 of CO_2, and 0·0715 of OH_2.
III. 0·1181 of substance gave 0·3018 of CO_2, and 0·0725 of OH_2.

These numbers give percentages agreeing with those required by the formula—

$$C_{12}H_{14}O_3 = C_6H_4(OCH_3)—C_3H_4—CO.(OCH_3).$$

	Theory.	Experiment. I.	II.	III.
Carbon	69·9	69·78	69·48	69·69
Hydrogen	6·79	6·75	6·82	6·82

This substance is therefore the methylic ether of an α-methylorthoxyphenylcrotonic acid, and may be called *methylic-α-methylorthoxyphenylcrotonate.*

This compound is a thick, colourless, highly refracting fluid. Its sp. gr. compared with water at the same temperatures is—

at 15°.... 1·1112 at 30°.... 1·1061

The boiling point is 274—275°, and its magnetic rotary power for the sodium line 2·232, water = 1; both of these are probably a little high from the presence of minute quantities of propionic coumarin in the substance used.

It does not appear to be easily changed into its isomeride by boiling. It dissolves in sulphuric acid with evolution of heat, and on diluting the mixture propionic coumarin separates out. Its isomeride, the β-ether, changes under these circumstances to a very thick oil, apparently in consequence of polymerisation.

α-Methylorthoxyphenylcrotonic Acid.

To obtain the acid from its methylic derivative, it was boiled with alcoholic potassic hydrate until quite miscible with water. This decomposition takes place easily. Water was then added, and the solution boiled until free from alcohol, and on being acidified with hydrochloric acid an oily acid separated, which soon solidified to a crystalline mass. This was collected, washed, dried between bibulous paper, and crystallised from petroleum spirit. It was then obtained in brittle feathery crystals. For further purification it was recrystallised from alcohol. The analysis of this body gave the following numbers:— .

I. 0·2615 of substance gave 0·6564 of CO_2, and 0·1472 of OH_2.
II. 0·2492 of substance gave 0·6276 of CO_2, and 0·1424 of OH_2.

These give percentages agreeing with the formula—

$$C_{11}H_{12}O_3 = C_6H_4(OCH_3)—C_3H_4—COOH.$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	68·74	68·45	68·68
Hydrogen.....	6·25	6·25	6·34

This acid may therefore be called *α-methylorthoxyphenylcrotonic acid.* It melts at 118°, whereas the β-acid melts at 107°. It does not appear to be converted into the β-acid by the action of light. It is freely soluble in alcohol, from which it separates in brilliant crystals, belonging to the oblique system. These have been measured, and are described at the end of this paper (p. 449). It is moderately soluble in hot petroleum spirit. It has no very decided taste at first, but after being in the mouth for some time, it produces a sensation of sweetness, continuing for a long time, and causing a flow of saliva.

With phosphoric chloride it yields propionic coumarin. The reaction may be written thus:—

$$\begin{array}{l} C_6H_4.(OCH_3) \\ | \\ C_3H_4 \\ | \\ CO(OH) \end{array} + PCl_5 = \begin{array}{l} C_6H_4 \\ | \\ C_3H_4O \\ | \\ CO \end{array} + CH_3Cl + HCl + PCl_3O.$$

When dissolved in concentrated sulphuric acid, it decomposes with formation of propionic coumarin.

The following comparison of the properties of the normal acid obtained from the hydride of methyl salicyl and propionic anhydride, now called β-methylorthoxyphenylcrotonic acid, and the α-acid from

propionic coumarin will show how greatly they differ from each other :—

	α-Acid.	β-Acid.
Melting point.....	118°.	107°.
Colour of ferric salt	A somewhat reddish-buff amorphous precipitate.	A yellowish-buff precipitate.
Colour of cupric salt.....	A pale bright yellow-green precipitate.	A pale bright blue precipitate.
Silver salt	A white precipitate, becoming crystalline in a short time.	A white precipitate.
Sodium salt.....	Deliquescent.	Not deliquescent.
Barium salt	Extremely soluble and drying up to an amorphous product.	Rather easily soluble in boiling water, but deposited, on cooling, in beautiful masses of fine needles, which when dry appear like asbestos.
With PCl_5	Yields propionic coumarin.	Yields the chloride of the acid radical.
With H_2SO_4	Yields propionic coumarin.	Yields an apparently polymerised acid.

α-Methylorthoxyphenylcrotonic acid when boiled with dilute hydrochloric acid for some time, decomposes, yielding an amorphous resinous product and an acid forming a soluble barium salt, but apparently not the β-acid.

With nitric acid both the α- and β-acids yield compounds giving bright red colours with alcoholic potassic hydrate.

α- and β-Methylorthoxyphenylcrotonic Acids and Nascent Hydrogen.

On placing sodium-amalgam in solutions of the sodium salts of these acids, scarcely any hydrogen is given off for an hour or more, or until the reaction is practically over. On acidifying the solutions, oily products separate in both cases, gradually solidifying and becoming crystalline.

They were separately converted into baric salts and twice crystallised. They had exactly the same appearance, were easily soluble in water, and appeared to contain water of crystallisation.

These salts were dissolved in water and decomposed with hydrochloric acid, and the acids crystallised from petroleum spirit. They

melted at the same temperature, and were evidently identical. Submitted to combustion, they gave the following numbers:—

I. 0·1517 of substance gave 0·3793 of CO_2, and 0·1028 of OH_2.
II. 0·2386 of substance gave 0·5929 of CO_2, and 0·1498 of OH_2.
III. 0·1111 of substance gave 0·2765 of CO_2, and 0·0726 of OH_2.

The substance used in analysis I was prepared from the β-acid, that from II and III from the α-acid.

These numbers give percentages agreeing with those required by the formula—

$$C_{11}H_{14}O_3 = C_6H_4(OCH_3)—C_3H_5—COOH.$$

	Theory.	Experiment. I.	II.	III.
Carbon.....	68·04	68·18	67·80	67·88
Hydrogen....	7·20	7·20	6·97	7·26

The acid is therefore *dihydromethylorthoxyphenylcrotonic* or *methylorthoxyphenylbutyric acid.* It melts at 55—56°. When strongly heated it distils, with but little decomposition, coming over as a colourless oil, which gradually solidifies to a crystalline mass on standing. It is extremely soluble in alcohol, carbon disulphide, and glacial acetic acid. From boiling petroleum spirit it gradually crystallises as it cools, usually in a confused state, but sometimes in transparent prisms. It is soluble to a small extent in boiling water, the solution becoming milky on cooling, but it separates out after standing in long transparent needles.

Baric Salt.—This was obtained by boiling the acid with a solution of baric hydrate, removing the excess of the latter with carbonic acid, boiling, filtering, and then evaporating the filtrate to a small bulk. The baric salt then came down in small transparent plates, which when seen under the microscope were somewhat like crystals of baric chloride; they also showed a fine play of colours with polarised light. It contains water of crystallisation, which is driven off at 100°.

0·1962 of substance dried at 100° gave 0·0867 of $BaSO_4$ = 25·98 per cent. Ba.

The formula $C_{22}H_{26}BaO_6$ requires 26·29 per cent. Ba.

It is moderately soluble in cold and easily in boiling water. With silver nitrate it gives a white apparently amorphous precipitate of the silver salt.

α- and β-Methylorthoxyphenylcrotonic Acids and Bromine.

Separate quantities of these two acids were finely powdered and exposed to the vapour of bromine in the dark for about 36 hours. Hydrobromic acid was formed, and the products after being kept

over potassic hydrate for some days, were found to have increased in weight, and become about two and a half times as heavy as they were originally. They were twice crystallised from chloroform, and thus obtained as a white crystalline powder. The products were identical, and gave the following numbers on analysis :—

I. 0·2030 of substance gave 0·1956 of CO_2, and 0·0374 of OH_2.
II. 0·2098 of substance gave 0·1955 of CO_2, and 0·0387 of OH_2.
III. 0·1624 of substance gave 0·1533 of CO_2, and 0·0296 of OH_2.

Nos. I and II were made from β-acid, No. III from α-acid. The percentages yield numbers leading to the formula—

$$C_{11}H_{10}Br_4O_3.$$

		Experiment.		
Theory.		I.	II.	III.
Carbon.....	25·88	26·23	25·41	25·74
Hydrogen....	1·96	2·04	2·04	2·02

This substance may be called *dibromide of dibromomethylorthoxyphenylcrotonic acid* or *tetrabromomethylorthoxyphenylbutyric acid.* It melts at about 200°. It is moderately soluble in boiling but only a little so in cold chloroform. In alcohol it is easily soluble, but evidently decomposes as the fluid becomes acid. It gradually decomposes when boiled with water.

It is not dissolved by cold aqueous ammonia, or only to a small extent, but it becomes more crystalline, apparently in consequence of the formation of an ammonia salt, and not of any decomposition, for if the mixture be acidulated with nitric acid and filtered, the filtrate is found to contain only a trace of bromine. If heat, however, be employed, the ammonium then attacks it, and a milky fluid results.

If left in contact with a 50 per cent. solution of pure sodic hydrate in the cold, it appears to be but little acted upon, very little bromine being removed, but if the mixture be diluted so as to form a clear solution, and then gradually warmed at about 40—45°, it begins to become milky.

Endeavours have been made to obtain dibromides of the α- and β-acids, and also their ethers, but no definite products have as yet been obtained. The constitution of this body is probably—

$$C_6H_2Br_2(OCH_3)—CHBr—CBr(—CH_3)—COOH$$

α-Methylorthoxyphenylcrotonic Acid and Hydriodic Acid (fuming).

This acid combines with hydriodic acid, sp. gr. 1·94, just as the β-acid does (*Chem. Soc. J.*, May, 1878), and the product, when treated

with sodic carbonate, yields orthoallylanisoïl, boiling at 222—223°, and having the sp. gr. at 30° of 0·989, numbers showing its identity with the product obtained from the β-acid.

β-Methylorthoxylphenylcrotonate of Methyl.

This body was prepared for the purpose of comparing it with its isomeride the α-product. It was made by converting the β-acid into its chloride with phosphoric chloride, and then gradually adding it to methylic alcohol. It was well washed with water, and then a little alkali, and afterwards dried and distilled, when most of it came over at 286°. On analysis it gave the following numbers:—

0·1462 of substance gave 0·3738 of CO_2, and 0·0898 of OH_2.

	Theory.	Experiment.
Carbon.....	69·9	69·72
Hydrogen.....	6·79	6·82

This ether is very like its isomeride, being a thick, highly refracting oil, its boiling point is, however, about 11° higher; it is also more dense, its specific gravity compared with water at same temperatures being—

at 15°.....	1·1279
at 30°.....	1·1136

PRODUCTS DERIVED FROM BUTYRIC COUMARIN.

Methylic α-Methylorthoxyphenylangelate.

Butyric coumarin was converted into the saline sodic derivative, and the compound treated with methylic iodide, as in the preparation of the analogous compounds from propionic coumarin, the proportion being varied to suit the different atomic weight of the body. In this manner a methylic ether was obtained, which on analysis gave the following numbers:—

I. 0·1446 of substance gave 0·3755 of CO_2, and 0·0932 of OH_2.
II. 0·1117 of substance gave 0·2896 of CO_2, and 0·0704 of OH_2.

From these results it is seen to have the formula—

$$C_{13}H_{16}O_3 = C_6H_4(OCH_3).C_4H_6.CO(OCH_3).$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	70·9	70·81	70·7
Hydrogen.....	7·27	7·23	7·0

It may therefore be called *methylic α-methylorthoxyphenylangelate.*

It is a thick, colourless, highly refracting fluid, boiling at 282°, and having a density of—

at 15°	1·1044
at 30°	1·0882

compared with water at the same temperatures. With concentrated sulphuric acid it decomposes with formation of butyric coumarin.

α-Methylorthoxyphenylangelic Acid.

The methylic ether just described is easily decomposed by boiling with an alcoholic solution of potash. The separation of the acid from the resulting potassium salt and its purification were performed in exactly the same way as in the case of the preparation of α-methylorthoxyphenylcrotonic acid.

On analysis it gave the following numbers:—

I. 0·2459 of substance gave 0·6325 of CO_2, and 0·1498 of OH_2.
II. 0·2556 of substance gave 0·6551 of CO_2, and 0·1544 of OH_2.

These numbers gives percentages leading to the formula—

$$C_{12}H_{14}O_3 = C_6H_4(OCH_3).C_4H_6—COOH.$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	69·9	70·1	69·85
Hydrogen	6·79	6·77	6·71

This may be called *α-methylorthoxylphenylangelic acid*. It melts at 88°. It is very easily soluble in alcohol, and crystallises from it after standing for some time in very beautiful transparent crystals. These have been examined, and are described at the end of this paper (p. 451). It is moderately soluble in boiling petroleum spirit. When tasted it produces the same effect of sweetness as the α-methylorthoxyphenylcrotonic acid, but not so distinctly.

With phosphoric chloride it yields butyric coumarin, thus:—

$$\begin{matrix} C_6H_4(OCH_3) \\ | \\ C_4H_6 \\ | \\ COOH \end{matrix} + PCl_5 = \begin{matrix} C_6H_4 \\ | \\ C_4H_6\ O \\ | \\ CO \end{matrix} + CH_3Cl + PClO + HCl.$$

With concentrated sulphuric acid it decomposes, with formation of butyric coumarin.

The following comparison of its properties with those of its isomeride obtained from the hydride of methylsalicyl and butyric anhydride, now called β-methylorthoxyphenylangelic acid, will show how much they differ from each other:—

	α-Acid.	β-Acid.
Melting point.....	88°.	105°.
Colour of ferric salt	Orange-brown.	Buff.
Colour of cupric salt.....	A bright yellow-green.	Pale blue-green.
Silver salt	A white precipitate, becoming crystalline; soluble in hot water, and separating in nodular masses of crystals on cooling.	An amorphous precipitate, soluble in boiling water, and deposited in an amorphous state on cooling.
Barium salt	Very soluble in water.	Much less soluble than the *a*-salt.

α- and β-Methylorthoxyphenylangelic Acids and Bromine.

Specimens of these acids were exposed to the action of bromine vapour in the dark for about 24 hours; they became sticky products, containing much free bromine. To remove this from them, they were kept over solid potassic hydrate, a few days after which they became much harder, and capable of being broken up. After this had been done they were again left over potassic hydrate for several days. They were then boiled with sufficient petroleum spirit (b. p. 100—130°) to dissolve them, filtered, and the solution allowed to stand. Crystalline products were deposited, and on analysis gave the following numbers:—

I. 0·1589 of substance gave 0·1591 of CO_2, and 0·0330 of OH_2.
II. 0·1540 of substance gave 0·1558 of CO_2, and 0·0352 of OH_2.

These lead to the formula—

$$C_{12}H_{12}Br_4O_3.$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	27·4	27·18	27·58
Hydrogen	2·29	2·30	2·54

The substance used in No. I was made from the β-acid, No. II from the α-acid. Both products are identical, although the crude substance obtained from the β-acid was easiest to purify, as it crystallised more freely.

This substance is the *dibromide of dibromomethylorthoxyphenylangelic acid*, or *tetrabromomethylorthoxyphenylvaleric acid*. It melts at about 159°, with decomposition. It is difficultly soluble in boiling

petroleum, and nearly insoluble in it when cold. It is deposited from it in minute transparent prisms.

Its constitution is probably—

$$C_6H_2Br_2(OCH_3)—CBr—CBr(C_2H_5)—COOH.$$

α- and β-Methylorthoxyphenylangelic Acids and Nascent Hydrogen.

Both these acids, when treated with sodium-amalgam, give a thick oily acid, which I have not been able to obtain in a fit state for analysis. It distils with but little decomposition. It gives a barium salt, forming minute crystals, very easily soluble in water. On analysis this gave 25·17 per cent. barium, theory requiring 24·86 for the formula $C_{24}H_{30}BaO_6$.

Methylic β-Methylorthoxyphenylangelate.

This ether was made by treating the chloride of the acid radical with methylic alcohol. It was not analysed. It is a thick, highly refracting oil, boiling at 292°, and having a density of—

at 15°..... 1·1100
at 30°..... 1·1008

The boiling point is therefore about 10° higher than that of the α-isomer; it is also more dense.

β-Ethylorthoxyphenylcrotonic Acid.

The preparation of this acid was undertaken for the purpose of making some comparisons between it and its isomerides. It was prepared from the hydride of ethyl-salicyl propionic anhydride and sodic propionate in the usual manner. These materials give a very good yield of this new acid. It was purified by crystallisation from alcohol, and gave the following numbers on analysis:—

I. 0·1781 of substance gave 0·4541 of CO_2, and 0·1084 of OH_2.
II. 0·1574 of substance gave 0·4030 of CO_2, and 0·0966 of OH_2.

These numbers give percentages agreeing with the formula—

$$C_{12}H_{14}O_3 = C_6H_4(OC_2H_5)—C_3H_4—CO(OH).$$

	Theory.	Experiment. I.	Experiment. II.
Carbon	69·9	69·53	69·85
Hydrogen.....	6·79	6·76	6·81

β-Ethylorthoxyphenylcrotonic acid melts at 133°. It is a beautiful acid, and crystallises in rather large tables or flat prisms, apparently right rhombic. It is easily soluble in alcohol.

Baric Salt. — On adding baric chloride to a hot solution of the ammonic salt of this acid, no precipitate forms, but on concentrating the baric salt separates out as thick oily drops; on cooling, however, the solution becomes filled with beautifully white satiny needles of this compound, not unlike benzoic acid; on adding these crystals to boiling water they partially dissolve and partially fuse. It is moderately soluble in cold, and rather easily so in boiling water. Sodic chloride precipitates it from its aqueous solution.

Methylic Methylparoxyphenylacrylate.

This substance was prepared for the purpose of comparing its boiling point with its isomerides. For this purpose methylparoxyphenylacrylic acid was treated with pentachloride of phosphorus, and the resulting chloride gradually added to methylic alcohol. After the reaction was over, the product on standing a short time began to deposit this ether in beautiful white plates. It was purified by recrystallisation from alcohol, and on analysis gave the following numbers:—

0·0958 of substance gave 0·2422 of CO_2, and 0·0549 of OH_2.

	Theory.	Experiment.
Carbon	68·75	68·95
Hydrogen	6·25	6·26

Methylparoxyphenylacrylate of methyl melts at 89°, and on cooling solidifies to a beautiful hard crystalline mass. It distils at 303°. It is easily soluble in boiling, and only moderately so in cold alcohol. It crystallises in rather large, irregular plates, very smooth to the touch. It will be observed that its boiling point is about 10° higher than its β-ortho isomeride.

Coumarins.

The following are the observed boiling points of these bodies made under the same conditions:—

Coumarin.....	290·0°
Propionic coumarin	292·5
Butyric „	299·0

The crystalline forms of the two last coumarins have been determined, and will be found at the end of this paper (pp. 446, 447).

Dr. Gladstone has been good enough to determine the refraction

equivalent of ordinary coumarin for me, and obtained the following results:—

A.....	71·17
D.....	73·22
H.....	83·29

A solution of ordinary coumarin in sodic hydrate (*i.e.*, α-sodic coumarate) when exposed to sunlight for some weeks, is partially changed, and when acidified gives coumarin mixed with about its own weight of β or ordinary coumaric acid, judging from its fusing point, &c.

From the foregoing results we see that acids isomeric with the already known methylorthoxylphenylcrotonic and angelic acids can be obtained from propionic and butyric coumarins, in the same way as α-methylorthoxyphenylacrylic acid is obtained from ordinary coumarin. These new α-acids, as I have called them, differ in a very marked way from the corresponding ordinary or β-acids, as the comparisons given in this paper show. They are, however, not so susceptible of change as the first member of the series, viz., α-methylorthoxyphenylacrylic acid, which, by the action of heat or light, soon becomes converted into the β-acid. This change I have not hitherto been able to effect with these two new acids, probably because I have not given sufficient time. There is also less difference between the boiling points of their methylic ethers and those of the β-acids, than between those of the α- and β-methylorthoxyphenylacrylic acids. This greater readiness to change, and wider difference of properties, as compared with their homologues, is apparently common to acrylic compounds. The hydrocarbons and anisoïls related to them as cinnamene, isopropylvinylbenzene, para- and ortho-vinyl anisoïl, also rapidly polymerise when exposed to the action of heat or light, their homologues not doing so, or only slowly, except when submitted to the action of chemical agents, such as sulphuric acid. The difference between their boiling points and that of their next homologue is also much greater than between the homologues above them, so that it is not surprising to find that α-methylorthoxyphenylacrylic acid should exhibit differences from the β-acid more marked than its homologues; but from the manner of formation of these acids from their coumarins, as well as from their properties, there cannot be any doubt that the isomerism existing between them and the corresponding β-acids is of the same kind as that between the α- and β-acrylic acids.

From the results which have been obtained, it appears generally that the effect of chemical action (unless of a feeble kind) on any part of α-methylorthoxyphenylacrylic acid or its homologues, is the formation of a β-compound or its derivatives. Thus, fuming nitric acid acting on the C_6-group of the acrylic acid converts it into a

β-dinitro-acid. Phosphorus pentachloride acting on the carboxyl group produces the chloride of the β-acid. Nascent hydrogen acting upon the C_2H_2, or analogous groups in the homologous acids, gives the same hydro-acids as the β-acids. Bromine in excess, acting on the C_6 and C_2H_2 or analogous groups, also gives the same product as the β-acid under similar circumstances. The explanation of this would appear to be that the heat evolved by the chemical action converted the α- into the β-derivative.

If, however, α-methylorthoxyphenylacrylic acid dissolved in chloroform or carbon disulphide be treated with a limited amount of bromine, a dibromide is obtained isomeric with the one produced from the β-acid under similar circumstances.*

The formation of these two compounds corresponds with the formation of the dibromides of maleic and fumaric acid, the bromine being connected with C_2H_2 in both cases, so that any argument based upon the one set of dibromo-compounds applies to the other.†

As maleic acid forms a dibromide different from that of fumaric acid, it is supposed that their isomerism rests on the $-C_2H_2-$ group, the arrangement of its elements in maleic acid being $-CH_2-\overset{\|}{C}-$, and in fumaric $-CH{=}CH-$, so that the dibromides would contain respectively $-CH_2-CBr_2-$ and $-CHBr-CHBr-$. Anschütz (*Ber.*, **10**, 1886) thinks that this order should be reversed.

But it is obvious that the fact of these acids forming isomeric dibromides does not necessarily require this explanation, as the dibromides may be isomeric simply because the acids themselves are so. Probably the amount of heat given out in their formation is not sufficient to change the maleic into a fumaric compound.

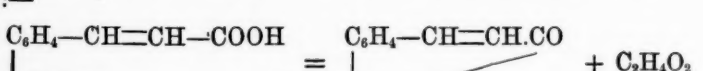
The hypothesis that the isomerism of these acids is dependent upon the two different arrangements in the C_2H_2 group is very difficult to accept, because it requires that its structure should change in opposite ways under the same influence. If a body contained the unsymmetrical group $-CH_3-\overset{\|}{C}-$ it would not be difficult to conceive that by the action of heat it might become symmetrical by changing into $-CH{=}CH-$, but that this group should by the very same influence turn back again to $-CH_2-\overset{\|}{C}-$ is very incomprehensible; but this view of the subject I think requires this to be believed, because maleic acid when heated is converted into fumaric acid, and this on further heating changes back, maleic anhydride and water being formed.

* In this reaction the amount of heat given out is very small compared with that given out when the acid is treated with nascent hydrogen from sodium amalgam.

† Baeyer has also referred to the isomerism of these acids as having a great resemblance to that existing between fumaric and maleic acids.

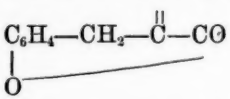
If we consider the relationship of ordinary, or as I for distinction sake will call it, β-coumaric, acid to the one obtained from coumarin, which I propose to call α-coumaric acid, the compounds of which were examined by R. Williamson (*Chem. Soc. J.*, 1875, 850), we find that the same or analogous changes take place by the action of heat on them.

When β-coumaric acid, or which is practically the same, aceto-coumaric acid* is heated, it splits up into coumarin and acetic acid, thus:—

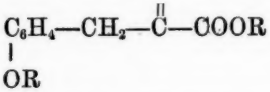


Aceto-coumaric acid. Coumarin.

In this decomposition we do not see anything to warrant us in supposing that the —CH=CH— group has changed, as it has had no part to play in the decomposition, and it is scarcely conceivable that it should have become unsymmetrical by the action of heat alone; but even supposing it had, and the constitution of coumarin thus became—



the α-coumarate would then be represented thus—



and on submitting this to heat, the very agent which previously was supposed to have changed the —CH=CH— into —CH_2—$\overset{\overset{O}{\|}}{C}$—, now makes it do the reverse, and by converting it into a β-coumarate, become again —CH=CH—.

From these considerations I do not think that this isomerism can be accounted for by this change of structure in the C_2H_2 group, nor do I see any other evidence of weight to support it. If this be so, and there is evidently no ground for supposing that any change of arrangement takes place in the other groups of which these bodies are constituted, then this isomerism cannot be explained by any ordinary kind of chemical constitutional formula we have at present.†

* The reason why aceto-coumaric acid yields coumarin, and coumaric acid does not, is, I believe, due to the phenolic hydrogen being replaced by acetyl, and thus keeping the decomposition to a single molecule of the acid, coumaric acid being so ready to form complex resinous products.

† By Van't Hoff's hypothesis it is possible to represent coumaric acid in two different ways. This, however, also refers to the C_2H_2 group.

This being the case, it will be interesting to refer to the physical facts for information, and see in which particulars these isomeric bodies differ from each other.

The following is a table showing the observed boiling points, which were all made in the same apparatus and with the same thermometer; also the specific gravities of the ethers of the acids described in this paper.

	B. p.	Diff.	Sp. gr.	Diff.	Refraction equivalents for A.	Refraction equivalents for H.	Dispersion equivalent.
Methylic α-methylorthoxyphenylacrylate, $C_{11}H_{12}O_3$.	275°	=18°	1·1404	·0082	93·42	107·58	14·16
Methylic β-methylorthoxyphenylacrylate, $C_{11}H_{12}O_3$.	293		1·1486		95·10	113·66	18·56
Methylic α-methylorthoxyphenylcrotonate, $C_{12}H_{14}O_3$	275	=11	1·1112	·0167	—	—	—
Methylic β-methylorthoxyphenylcrotonate, $C_{12}H_{14}O_3$	286		1·1279				
Methylic α-methylorthoxyphenylangelate, $C_{13}H_{16}O_3$.	282	=10	1·1044	·0056	—	—	—
Methylic β-methylorthoxyphenylangelate, $C_{13}H_{16}O_3$.	292		1·1100				
Methylic β-methylorthoxyphenylacrylate, $C_{11}H_{12}O_3$.	293	=10	—	—	—	—	—
Methylic β-methylparaorthoxyphenylacrylate, $C_{11}H_{12}O_3$	303						

From this we see that the difference between the boiling points of the α- and β-methylic ethers is very large, in the case of the first member of the series no less than 18°, and in the other instances 10° and 11°, an amount as great as that between the β-ortho- and para-methylic ethers given at the bottom of the table. The boiling points of the α-compounds it will be observed are always the lowest.

If we compare the densities, we invariably find the α-products to be lower than the β. This difference is probably somewhat greater than the determinations indicate, for in the case of methylic α-methylorthoxyphenylacrylate, there is a certain amount of the β-ether produced when it is rectified to remove impurities; it is also likely to contain a small quantity of coumarin. These products would increase its density. The other ethers also usually contain small quantities of the coumarins they have been prepared from, which also would increase their densities.

The magnetic rotary power of the methylic α- and β-methylorthoxyphenylacrylates shows a difference in the same direction, the α giving a lower result than the β, considerably greater than the variations of the densities would account for.

Dr. Gladstone's results show the same to hold good in the case of their refractive power.

These facts would seem to indicate that in the α-compounds the groups, or some of them, contained in the molecules are *farther apart* than in the latter β-compounds.*

Should this be so, in what way would the properties of the α-bodies be expected to differ from the β? One would imagine that any group or groups, being less intimately connected, would be more easily dissociated, and therefore that these bodies should be the least stable of the two.

There is no doubt that the α-bodies are very much less stable than the β. For example, α-coumaric acid cannot exist in the free state for any appreciable length of time, but splits up into coumarin and water. The same is true of its homologues. The α-methylated acids and their ethers, although moderately stable, are not so stable as the corresponding β-compounds. Thus α-methylorthoxyphenylcrotonic and angelic acids and their ethers, when treated with phosphoric chloride yield their coumarins, whereas the β-acids yield the chlorides of their radicals.

There is one point connected with this matter of isomerism worthy of note, and that is, that the changes of condition these bodies undergo are always associated with *dehydration* and *rehydration*. Thus β-coumaric acid on losing the elements of a molecule of water, becomes coumarin. This when hydrated does not go back to β-coumaric acid, but to its unstable isomeride α-coumaric acid, and it is not until this (or rather its salt) is heated strongly that the original acid is reproduced. This suggests the thought, that if the α-bodies differ from the β- owing to a difference of distance between the groups in the molecules, does this difference of proximity exist between all the groups, or only between some? The above observations respecting their formation would make it appear that it was only between the radical and the hydroxyls, as it is first seen on hydrating the cou-

* In the recently published new edition of Part III of "Miller's Chemistry," I find the following statement (p. 993) at the end of Chapter X, in which the Van't Hoff hypothesis of isomerism is discussed, and the insufficiency of this and of the ordinary hypothesis is pointed out:—"Are we not perhaps justified in supposing that there are two classes of isomerides—ordinary isomerides, in which the atoms occupy relatively different positions—and exceptional isomerides, in which the atoms occupy relatively similar positions, but in which they are situated at different distances?"

marins. The difference of stability is also seen to be in connection with the hydroxyl.

These remarks also apply to the cases of maleic and fumaric acid, and citraconic and mesaconic acids, where we find the formation of maleic or citraconic acids resulting from the removal of a molecule of water from fumaric or mesaconic acids, and rehydration of the product. Maleic acid also appears to be less stable than fumaric, inasmuch as it is dehydrated by acetylic chloride, this reagent not acting on fumaric acid.*

It may be remarked in passing, that nearly all the bodies which are now called physical isomerides are hydroxylised products, and those containing the largest number of hydroxyls have the largest number of these isomerides, as in the case of the carbohydrates. Amongst the inorganic hydrates there are apparently isomeric bodies. Perhaps the soluble silicic acid, ferric oxide, and other analogous bodies are such. I hope to examine further into these peculiar kinds of isomerism from this point of view.

The formula I gave to phenylangelic acid some time since has been objected to by Fittig (*Annalen*, **195**, 169), also by Baeyer (*Ber.*, **13**, 115). It is the formula originally given to this body by Fittig and Bieber. Fittig and also Conrad and Bischoff (*Annalen*, **204**, 182), likewise believe that the formula of phenylcrotonic acid should be the same as that which I proposed for the isophenylcrotonic acid from oil of bitter almonds and succinic anhydride. From the new facts which have been brought to bear on these subjects, I am quite inclined to believe in the conclusions they have arrived at, viz., that phenylangelic acid should be represented as—

$$C_6H_5—CH=C<\begin{matrix}CH_2—CH_3\\COOH\end{matrix},$$

and phenylcrotonic as—

$$C_6H_5—CH=C<\begin{matrix}CH_3\\COOH\end{matrix}.$$

The analogous acids described in this paper would of course be similarly constituted. I am making some experiments on the phenylcrotonic and angelic acids and their bromine addition-products, which will I hope go to settle the formulæ of these acids. It is evident that if their constitution is correctly expressed above, they cannot yield homologues of propiolic acid.

As the coumarins and the α- and β-acids described in this paper form definite crystals, it was thought that their measurement would

* In one point maleic and fumaric do not correspond with the acids treated of in this paper, and that is in the boiling points of their ethers: that of maleic acid being higher than that of fumaric.

be of special interest, first, because they are homologues, and it was hoped that some relationship might be seen for the difference of CH_2; and secondly, the α and β being physical isomerides, it was also hoped that some definite crystallographic relationship between them might be discovered.

Mr. L. Fletcher of the British Museum very kindly undertook the measurement of the crystals, and has examined all the following bodies, so we now have the following series (ordinary coumarin having been previously examined) :—

Coumarin.
α- and β-Methylorthoxyphenylacrylic acids.
Propionic coumarin.
α- and β-Methylorthoxyphenylcrotonic acids.
Butyric coumarin.
α-Methylorthoxyphenylangelic acid.

I am sorry that I have not been able to get the β-methylorthoxyphenylangelic acid in a suitable state for measurement at present, and thus complete the series.

The following are Mr. Fletcher's results and observations :—

PROPIONIC COUMARIN.

System, Orthosymmetric or Rhombic.

Parameters :—$a : b : c :: 2{\cdot}1950 : 1 : 0{\cdot}4001$.

$110{\cdot}100 = 65° 31'$; $011{\cdot}010 = 68° 12'$; $101{\cdot}001 = 10° 20'$

Forms observed :—a 100, b 010, n 101, g 610, p 111, d 121.

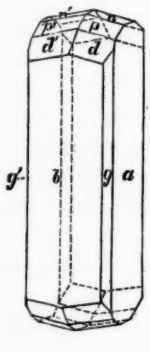


FIG. 1.

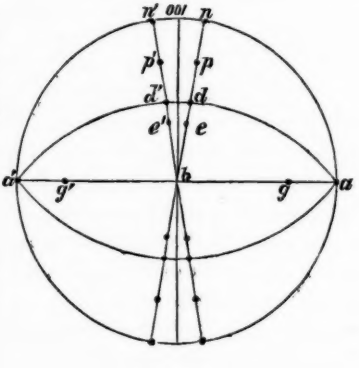


FIG. 2.

The faces b are generally very prominently developed.

The only angles which could be measured with sufficient accuracy

to serve for the determination of the parameters were: *ag*, *ad*, *pd*, *db*. From observation of these angles on seven crystals the most probable values of the parameters were calculated by the method of least squares.

Angles.	Calculated.	Observed. Mean of best angles.	Observed. Limits.
ag	20° 6′	20° 0′	19° 50′—20° 9′
ad	81 54	82 4	81 23—82 41
pd	16 44	16 36	15 40—17 41
db	51 47	51 48	51 19—52 8

A crystal of a second lot presented a similar habit to that figured above: on closer examination, however, it proved that the prominent pyramidal form instead of being *d* or (121) was *e* or (131), a form not observed on the first crystals.

Butyric Coumarin.

System, Monosymmetric or Oblique.

Parameters:—XOZ = 67° 18′; $a : b : c :: 1{\cdot}192 : 1 : 0{\cdot}694$.

001·100 = 112° 42′; 110·010 = 42° 17′; 011·010 = 57° 22′.

Forms observed:—*a* 100, *m* 110, *c* 001, *p* 111, *w* 430.

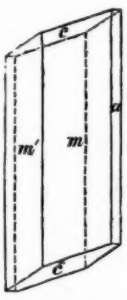


Fig. 3.

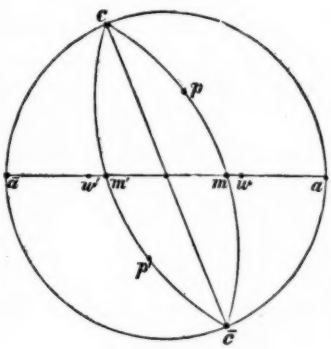


Fig. 4.

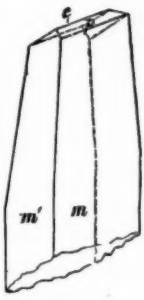


Fig. 5.

The crystals were very fragile, and often hollow; generally the summits were broken: no doubly-terminated crystal was discovered. The forms *mac* were occasionally well developed, as in Fig. 3; while very often the faces *mm'* were curved in the zones *mc*, *m'c*, as shown in Fig. 5; on one crystal a small but distinct plane *p* was observed, but as no image could be obtained the angle was determined by means of

the position of maximum reflexion on observation with the micro-telescope; on this crystal the faces mm' were curved through angles varying from 5—20°. The form w was only imperfectly developed.

Angles.	Calculated.	Observed.
mm'.....	84° 34′	84° 34′
mc	105 3	105 3
mp	57 53	57 53
mw	8 12	7 52

α-Methylorthoxyphenylacrylic Acid.

System, Monosymmetric or Oblique.

Parameters:—XOZ = 87° 12′; $a : b : c$ :: 0·677 : 1 : 1·122.

001·100 = 92° 48′; 110·010 = 55° 56′; 011·010 = 41° 45′.

Forms observed:—a 100, r 102 curved, p 111, l 011, m 110.

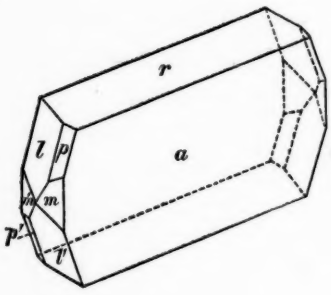


Fig. 6.

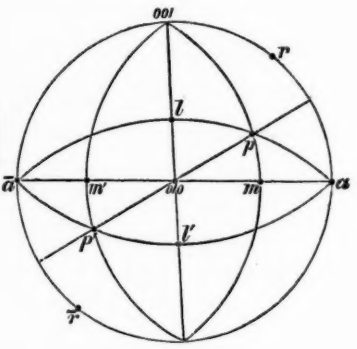


Fig. 7.

Angles.	Calculated.	Observed.
ma.....	34° 4′	34° 4′
$l\bar{l}'$	96 30	96 30
al	91 52	91 52
$p'p$.....	118 46	118 58
pm.....	27 1	26 56
ap	43 2	42° 24′—43° 18′
lp	48 50	48° 50′
lm	66 59	66° 49′—67° 19′
lp'	84 12	84 6½—84 11½
$p'm$	108 41	108 23—108 40
ar	52 2	curved from 50 41 to 53 30

A larger crystal of a second growth presented a very different aspect, owing to the disappearance of the form r (102), and to the intersection of the planes $l\bar{l}$ in an edge, as in the crystals of the corresponding β-acid next described.

β-Methylorthoxyphenylacrylic Acid.

System, Monosymmetric or Oblique.

Parameters:—XOZ = 64° 41′; $a : b : c$ :: 0·444 : 1 : 0·807.

001·100 = 115° 19′; 110·010 = 68° 7′; 011·010 = 53° 54′.

Forms observed:—a 100, b 010, m 110, l 011.

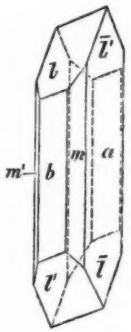


Fig. 8.

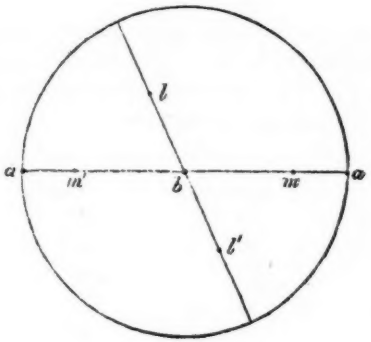


Fig. 9.

The crystals are generally tabular through the large development of the faces of the form a.

Angles.	Calculated.	Observed.
mb	68° 7′	68° 11′
$m\bar{m}'$	43 46	43 45
la	110 13	109° 41′—110° 53′
$l\bar{l}'$	72 12	72 13 — 72 8
lb	53 54	53 54 — 53 32
lm	95 43	95 48 — 96 0

α-Methylorthoxyphenylcrotonic Acid.

System, Monosymmetric or Oblique.

Parameters:—XOZ = 64° 54′; $a : b : c$ :: 0·863 : 1 : 1·252.

001·100 = 115° 6′; 110·010 = 52° 0′; 011·010 = 41° 25′.

Forms observed:—c 001, m 110, l 011, n 101, k $\bar{1}$01.

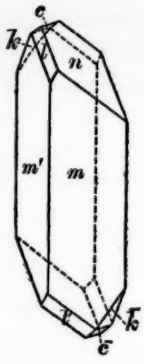


FIG. 10.

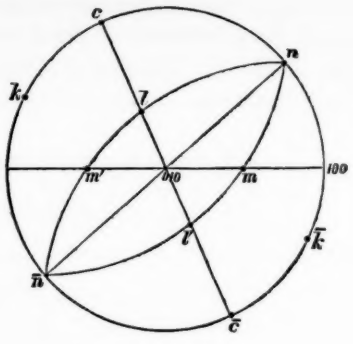


FIG. 11.

Many of the crystals were greatly distorted, the angles between faces which ought to have been parallel being in some cases as much as 2° or 3°. The following observed angles are deduced from the measurement of ten crystals:—

Angles.	Calculated.	Observed. Means.	Observed. Limits.
nc	73° 42′	73° 42′	73° 11′— 74° 38′
ck	39 8	39 8	38 49 — 39 25
mm′	104 0	104 0	103 55 —104 9
cl	48 35	48 6	46 27 — 49 40
mn	53 46	53 43	51 37 — 54 5
nl	79 18	79 33	76 59 — 81 23
lm′	46 56	—	45 50 — 48 19

β-METHYLORTHOXYPHENYLCROTONIC ACID.

System, Monosymmetric or Oblique.

Parameters:—XOZ = 84° 18′; $a : b : c :: 1{\cdot}281 : 1 : 0{\cdot}762$.

001·100 = 95° 42′; 110·010 = 51° 53′; 011·010 = 52° 49′.

Forms observed:—*a* 100, *v* 320, *m* 110, *n* 101, *c* 001, *p* 111, *g* 122, *l* 011.

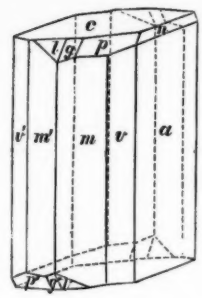


FIG. 12.

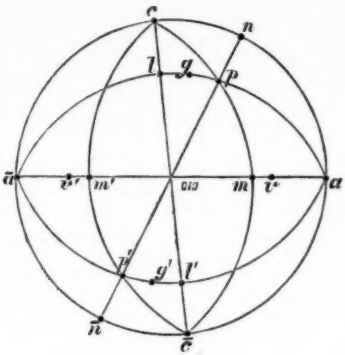


FIG. 13.

All the forms were well developed. The crystals were frequently twinned about the plane 100.

Angles.	Calculated.	Observed.
av	40° 22′	40° 37′—40° 55′
mv	11 31	9 53—11 40
vm′	87 45	86 54—87 56
ac	95 42	95 30—95 58
a′l	85 42	85° 32′
lg	13 23	13 28
gp	12 22	12 17
pa	68 23	68 23
cg	40 4	40 4
cl	37 11	37° 8′—37° 20′
cp	45 38	45° 34′
an	63 31	63 30

α-METHYLORTHOXYPHENYLANGELIC ACID.

System, Monosymmetric or Oblique.

Parameters:—XOZ = 75° 38′; $a : b : c :: 1{\cdot}607 : 1 : 1{\cdot}963$.

001·100 = 104° 22′; 110·010 = 32° 43′; 011·010 = 27° 44′.

Forms observed:—*a* 100, *m* 110, *c* 001, *n* 101, *s* $\bar{1}11$.

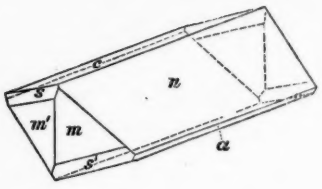


Fig. 14.

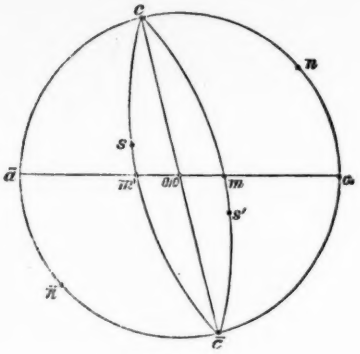


Fig. 15.

Angles.	Calculated.	Observed.
$m\bar{m}'$	65° 26′	65° 26′
nc	61 5	61° 2′—61° 5′
$m'c$	82 18	82° 16′
$m's$	22 27	21 12 (about)
mn	66 50	66 50

The results of the further investigation of the crystalline form of ordinary coumarin, and the β-methylorthoxyphenylangelic acid, as also of the optical series, Mr. Fletcher hopes to communicate at some future time to the Crystallological Society, a prominent object of which is the discovery of relations existing between the composition and the geometrical and physical properties of crystals.

LIX.—*The Alkaloïds of Nux Vomica.*

By W. A. Shenstone.

In a paper read before the Pharmaceutical Society (*Pharm. Journ.*, December 8th, 1877), I mentioned some substances which apparently had been produced by the action of water containing a very small proportion of acetic acid on brucine heated with it, in the course of attempts to free the brucine from strychnine by crystallising from hot aqueous solutions containing small quantities of its acetate.

On endeavouring to obtain the same products on a large scale from another specimen of commercial brucine, I was only partly successful, and thinking my former results might have been due to some difference in the alkaloïd, as for instance the presence of impurities, I decided that it would be well to prepare a specimen of brucine by a process so devised that heating should be avoided as far as possible, and heating with alkalis or acids altogether. It then seemed to me that, as the researches on which our present knowledge of the alkaloïds of nux vomica is based, were made with material which had been prepared by the old processes, and, as it is quite certain that these alkaloïds are much affected by saponifying agents, it would be well to take the opportunity of re-examining at least brucine, which is most readily attacked. I also thought that by making my examination as exhaustive as possible, I might hope to do something more towards finally setting at rest the question of the existence of a third alkaloïd, *igasurine*, in nux vomica seeds.

With the kind aid of Messrs. Hopkins and Williams, 56 lbs. of the seeds of *Strychnos nux vomica* were powdered, exhausted with alcohol, to which one-sixth part of water had been added, and the bulk of the spirit recovered. The product, in the form of a not very thin extract, was mixed when cold with 4 gallons of water, containing three-tenths per cent. of sulphuric acid, which dissolved the alkaloïds, leaving the greater part of other organic substances behind.*

The acid solution separated from the undissolved matter was mixed with excess of sodium carbonate, and after a few hours the precipitate was collected. The mother-liquors, which retained a large quantity of alkaloïd, were examined fully by a process which will be described later.

* This method was adopted after repeated trials on a small scale, which showed that, on account of the large amount of mucilaginous substances in the seeds, a tolerably economical method of extraction without the use of spirit was impossible, and of course the use of alcohol made it necessary to remove it subsequently by heat, as brucine is very freely soluble in that liquid.

The precipitate produced by potassium carbonate was dissolved in chloroform, and the solution extracted by thoroughly washing with water to which sulphuric acid was added gradually during the process, the first washing being withdrawn whilst still alkaline, in order to avoid crystallisation, which was apt to occur rather easily with strong and at the same time acid solutions; the subsequent washings were made with excess of acid. The solution of brucine sulphate thus obtained was still far from pure, and when alkalis were added to it in the ordinary way, gave a very unsatisfactory precipitate; but when the solution was placed in a shallow dish with a beaker containing some diluted solution of ammonia in the centre, and the whole was covered up pretty closely, the gradual action of the ammonia caused the alkaloïds to separate in crystals, which it was easy to deal with afterwards. The portion of the bases which had been got in the crystalline state in this manner was treated with dilute spirit, to dissolve the brucine, and the solution allowed to evaporate spontaneously. A crystalline mass of brucine then remained, which still contained much strychnine; it was dissolved in dilute sulphuric acid, added in such quantity as to leave a faintly alkaline solution, and precipitated with potassium iodide; the hydriodide of brucine was recrystallised as often as necessary from alcohol; and finally the alkaloïd was regenerated by agitating the solid hydriodide with solution of sodium carbonate, and shaking up with chloroform; finally the chloroform solution was extracted with dilute acid, and the base precipitated with ammonia.

This mode of purification answered admirably. *The brucine obtained did not yield any evidence of the presence of strychnine, when it was treated with diluted nitric acid, and the product examined for that substance*, thus confirming the results previously obtained on distinct lines of experiment, by A. J. Cownley (*Pharm. Journ.* [3], vi, 841) and myself, when we examined the alleged conversion of brucine into strychnine by the action of nitric acid (Sonnenschein, *Pharm. Journ.* [3], vi, 201, &c.), and it easily yielded the acetate in crystals on spontaneous evaporation of a solution of the base in acetic acid. This salt has been previously described as existing only as a gummy residue (probably owing to traces of impurity in the alkaloïd from which it was prepared); it is not very stable, quickly showing a slight change of colour.

Having now found a means of preparing brucine free from strychnine, and otherwise in a pure state, by a process which seemed to guarantee that the alkaloïd had not undergone change during its preparation, I made the following analyses:—

I. 0·0865 gram gave 0·2205 gram of carbonic acid, and 0·0516 gram of water.

II. 0·2864 gram burnt with copper oxide and a coil of freshly reduced copper in a Sprengel vacuum, gave 0·020697 gram of nitrogen.

The percentages corresponding to these numbers are discussed with others a little later.

As the alkaloïds which remained in the mother-liquor when the greater portion was in the first instance precipitated by sodium carbonate were considerable in quantity (90 grams), and as they would contain, besides the brucine and strychnine, the third alkaloïd, if there be one, I examined the bases from this portion very carefully, by the following method. The alkaline liquid was washed with chloroform till it was free from bitterness, and no longer gave any precipitate with tannin; the chloroform solution obtained was extracted with acid as before; the acid solution precipitated by exposure to ammoniacal fumes, and the brucine dissolved from the product with dilute spirit. The alcoholic solution yielded the greater part in crystalline form on spontaneous evaporation, but a quantity remained in the aqueous mother-liquor, which could be partly removed by washing with chloroform, and partly not. I will speak of these three fractions separately.

1. The crystalline portion was converted into hydriodide, recrystallised from alcohol, and regenerated as before, but with this difference, that the final precipitation with ammonia of a large part of it was done fractionally, so as to yield the alkaloïd in three fractions, A—1, A—2, A—3, a small portion (1·5 per cent.) remaining in solution; this part was only examined qualitatively. It exhibited no point of difference from the rest.

On combustion the three fractions gave the following numbers:—

III. 0·1320 gram A—1 gave 0·3374 gram CO_2, and 0·0798 gram H_2O.

IV. 0·1716 gram A—2 gave 0·4376 gram CO_2, and 0·1021 gram H_2O.

V. 0·1784 gram A—2 gave 0·4572 gram CO_2, and 0·1048 gram H_2O.

VI. 0·1625 gram A—3 gave 0·4141 gram CO_2, and 0·0957 gram H_2O.

2. The portion of the alkaloïd extracted by chloroform from the aqueous mother-liquor of the portion which crystallised, after purification by recrystallising the hydriodide and regenerating in the manner described, was dried at 105—107°, and analysed.

VII. 0·1060 gram gave 0·2719 gram CO_2, and 0·0634 gram H_2O.

The percentages corresponding to these various analyses stand as follows:—

	C.	H.	N.	O.
I	69·52	6·62	—	—
II	—	—	7·2	—
III	69·70	6·71	—	—
IV	69·54	6·60	—	—
V	69·89	6·50	—	—
VI	69·49	6·54	—	—
VII	69·95	6·64	—	—
Mean	69·68	6·60	7·2	16·52

The accepted formula for brucine, $C_{23}H_{26}N_2O_4$, requires—

C.	H.	N.	O.
70·0	6·64	7·1	16·26

Two determinations of platinum in platinum salt gave the following results:—

VIII. 0·4032 dried at 100—102°, gave 0·0654 of Pt.
IX. 0·4067 „ „ „ 0·0660 of Pt.

corresponding in each case to 16·22 per cent. of Pt. The present formula requires 16·43 per cent. of Pt.

Three determinations of iodine in hydriodide gave respectively 24·47 per cent., 24·25 per cent., 24·33 per cent. Mean, 24·38 per cent. The accepted formula requires 24·34 per cent. of iodine.

The results of these various analyses leave no doubt that the formula $C_{23}H_{26}N_2O_4$, already accepted, is correct, and hence it appears that brucine employed by previous experimenters prepared by the old processes, was not a saponification product of the alkaloïd present in the seeds, nor mixed with any such substances, but that the alkaloïd in the seeds is identical with that which they obtained. I have found in experiments described further on, that brucine is without doubt profoundly affected by heating with acids, alkalis, or even water, but with one exception the products are amorphous, resin-like bodies, from which unaltered brucine is easily separated in a pure state. I have little doubt, however, that the ordinary processes are very wasteful, from the following facts:—From 56 lbs. of nux vomica seeds in the above operations, I obtained in all a little more than 20 oz. of mixed crystalline, though not perfectly pure alkaloïds, an amount corresponding to above $2\frac{1}{4}$ per cent. The recorded proportions of brucine and strychnine, taking the improbable event of both being at their maximum, is 1·5 per cent. in all (*Pharmacographia*), so that my yield was cer-

tainly some 33 per cent. above that previously recorded, and perhaps exceeded it still more. On the other hand it is questionable whether the troublesome nature of my process would not take from it any advantage it may possess when applied on a large scale.

3. *Igasurine.*—The work detailed in the preceding pages gives account of the portion of alkaloïd precipitated by alkalis from the original solution in dilute acid, and of those portions of that which remained in the alkaline liquid, which, after separating strychnine, either crystallised on evaporation of the alcoholic solution, or were extracted afterwards from the mother-liquor of the crystallised portions by chloroform. It will be observed, on examining the results of analyses quoted on page 456, that these fail to give any indication of the presence of anything among them having a composition different from that of brucine. There remains, however, for consideration the contents of the mother-liquor, from which everything that chloroform would extract had been removed. This liquid gave on slow evaporation good-sized brown crystals, of a substance which, from its apparently definite character, puzzled me a good deal for a time. It appears to be very similar to a substance which, for the sake of distinction, I called a "new brucine salt," in a slight notice of a very small quantity of it obtained a few years ago (*Pharm. Journ.*, Dec., 1877).

It forms in good-sized crystals from impure solutions, but I have failed to get them so large after recrystallising; as it is freely soluble in warm water and alcohol, and less so in the cold, it can be easily purified by recrystallising, when it has a pale straw colour, which is not removed by further similar treatment; addition of alkalis to the aqueous solution gives a white precipitate; the substance is strongly reddened by nitric acid. Analysis gave the following results:—

I. 0·1742 gram dried at 100—105° gave 0·4018 gram of CO_2 and 0·1002 gram of water, corresponding to 62·7 per cent. of C, 6·3 per cent. of H.

II. After recrystallising, 0·1172 gram dried as before, gave 0·2685 gram of CO_2 and 0·07140 of H_2O.

III. 0·1802 gram gave 0·4115 gram CO_2 and 0·1102 gram H_2O, corresponding to—

	C.	H.
II	62·47	6·77
III	62·2	6·79

These analyses were made with potassium chromate for absorbing nitrous fumes, as first proposed by Perkin; probably, therefore, they are not quite trustworthy, as I did not find that process work very well, and had some difficulty in effecting complete absorption. I quote them, however, as they agree rather closely with those required for the

g and *h* igasurines of Schützenberger, coming between the percentages required for the two formulæ.* It seems very likely that the various igasurines of this experimenter were bodies like this, which, as I shall presently show, is almost certainly nothing but brucine with some very persistent impurity. When a portion was rendered alkaline and extracted with chloroform, as much as 89·7 per cent. was taken up by the chloroform. In order to examine the base, several grams were dissolved in water, and potassium iodide was added to the solution. A copious precipitate fell which was purified by recrystallising from spirit and regenerated; it was then found to contain 70·8 per cent. of C, and 6·42 per cent. of H. As it had a slightly brown colour, the product was again converted into hydriodide, crystallised, and the base regenerated and analysed.

0·1218 gram gave 0·3135 gram CO_2 and 0·0750 gram H_2O, corresponding to 70·19 per cent. of C and 6·8 per cent. of H.

These numbers correspond so closely with those required for brucine, that there is no doubt as to the nature of the base. I may add that its reactions agree precisely with those of brucine. The proportion of base extracted by chloroform was so high, and the proportion of carbon and hydrogen so much lowered by the small amount of other substances present, that it was hard to imagine this could be a definite compound of brucine with any organic acid; I am more inclined to think that the 89·7 per cent. taken up by chloroform still included some impurity, but I had not material enough to decide the point. Notwithstanding this opinion, I made careful search with the object of detecting any definite acid constituent, by treating with acids and distilling, and by extracting acidified solutions with ether and other solvents; I met with no success, however. I also examined the action of solutions of it on various metallic salts; but although it gave a precipitate with copper salts, the amount was too inconsiderable to offer any hope of obtaining any results in that direction. In concluding my remarks on this substance, I may say that it seems to me exceedingly likely that the workers who have supposed nux vomica seeds to contain a third alkaloïd, have been misled by bodies of analogous nature to this. As regards the work of Schützenberger, I have already written. As regards that of Desnoix, I may add that his methods of purification would cope but very imperfectly with such a substance as this.

It will be perceived that these various results fail to confirm the presence of any third alkaloïd. Of course it may be argued, that in the course of purification for analysis I may have overlooked such a

* *g* Igasurine, 62·37 per cent. of C; 6·9 per cent. of H.
h Igasurine, 62·68 per cent. of C; 6·47 per cent. of H.

body. This could be urged against any process whatever, especially any process that has to deal with a body accompanied by so much foreign matter as brucine and most alkaloïds are. On the other hand, I had, by exhausting the mother-liquors, which might be expected to contain igasurine, 90 grams of crude but crystalline alkaloïds dried only by pressing in calico. After working this up, I found that I could account for slightly under 82 grams, showing a loss of 8 grams, against which was a loss in the purification of the last product; and further, a part of it remained mixed with resinous impurity from which it could not be separated, certainly weighing several grams in all, though I did not weigh it, owing to an interruption in my work at the time. Had there been anything present of different nature to brucine or strychnine, I do not think I could have overlooked it.

The experiments I have been describing were undertaken in consequence of an opportunity presenting itself from the necessity I was under of preparing brucine by a method that should certainly not yield saponification-products in its place, or mixed with it, in order to obtain trustworthy results in examining the action of acids or alkalis upon it.

The results I have arrived at have satisfied me that the brucine of commerce, though sometimes not perfectly pure, does for the most part consist of brucine, and I am confirmed in this opinion by the fact that I have since obtained from commercial brucine a product similar to that yielded by my own alkaloïd when acted on by alcoholic soda, which reagent only has yielded any results of interest.

It was my intention to have extended my experiments with saponifying agents to strychnine; various obstacles, however, delayed me a good deal, and meanwhile experiments with that substance have been made by Gal and A. Étard (*Bull. Soc. Chim.* [2], **31**, 98), who, by the action of baryta-water, have obtained, not products such as those obtained by Wright, Ladenburg, and others from several alkaloïds, but very oxidisable bodies, $C_{21}H_{26}N_2O_4$ and $C_{21}H_{28}N_2O_5$, formed respectively by the assumption of two and three molecules of water, which differ from strychnine in their colour reactions, and whose gold and platinum salts are not stable. As their work does not appear to have extended to brucine, I have been much interested at the result of my previously projected experiments in this case.

When brucine was heated with water, aqueous potash, or dilute sulphuric acid in sealed tubes to various temperatures and for various times, nothing further was obtained on examining the products than unaltered alkaloïd, small quantities of yellow slightly basic varnishes which did not yield crystalline salts, and mother-liquors which underwent rapid oxidation on exposure to air. Examination for acids by acidification and distillation, or treatment of the acidified solutions with ether and other such solvents, gave no results. When, however,

alcoholic soda was employed, there was obtained a substance rather soluble in water which, after preliminary trials, was prepared as follows:—

About 60 grams of commercial brucine was placed with 600 c.c. of 5 per cent. alcoholic soda in a copper bottle securely closed, and was heated in a bath of boiling water for twelve hours. The contents of the bottle were then diluted with spirit and treated with carbon dioxide to remove the alkali, filtered, and the filtrate exposed that the spirit might evaporate. There remained a mass of black varnish-like substance containing numerous minute crystals; this was treated with the smallest possible quantity of water to form a sort of syrup, and filtered, and the residue was washed with as little water as possible. In this way I obtained a little over 7 grams of a grey crystalline powder, considerable loss having occurred in securing it. Various methods of purification involving recrystallisation having failed, in consequence of the instability of the substance in solution, it was dissolved in a very small quantity of water with dilute hydrochloric acid, filtered quickly, precipitated with ammonia, and washed with distilled water. Two such treatments yielded the body not absolutely pure, but very nearly so, and in as pure a state as was practicable, since the solution in acid visibly underwent change if left more than two or three minutes. About $2\frac{1}{2}$ grams were secured in nearly colourless microscopic crystals, which were quite stable in the dry state, with the following distinct characters. They were not reddened by nitric acid, but dissolved to a pale bright yellow liquid; if strong acid is used this, on dilution, gives no further result with stannous chloride than decolorisation, but if *boiled* with dilute nitric acid the solution gives a wine-red coloration on addition of stannous chloride, much fainter, however, than that given by brucine when similarly treated. On exposure of an ammoniacal solution to the air for a few hours, it acquires a purple colour, which becomes green later, but is changed to purple again by dilution; on adding an acid to this, a fine deep green is developed. Bromine-water added gradually produces a precipitate; if, when excess has been added, heat is applied, the colour due to bromine gradually goes till the boiling point is reached; there is then suddenly developed a fine magenta-red which is destroyed by stannous chloride, but is permanent for several days at least in air. Brucine similarly treated gives first a very transient pink, no precipitate, and, finally, on boiling well, developes a lighter shade of same red colour, the two actions being quite distinguishable.

It contains nitrogen, and gives a gold salt, which undergoes reduction almost at once, and a platinum salt, which, though more stable, is not sufficiently so for analysis; this platinum salt is rather soluble in water, and the mother-liquor deposited handsome red microscopic

crystals, which were seen to contain here and there a few small pale yellow crystals. All attempts to obtain crystalline salts of it by solution in acids failed, only yellow varnishes being produced, which quickly underwent oxidation on exposure. I was unable to attempt to prepare any salts by methods of precipitation for want of material.

Portions were dried at 100° C. and analysed:—

I. 0·1227 gram gave 0·2970 gram CO_2 and 0·0791 of H_2O.
II. 0·1391 „ 0·3364 „ CO_2 „ 0·0865 of H_2O.

		Theory for $C_{23}H_{28}N_2O_5$.	Found.		Mean.
C_{23}	276	66·99	66·01	65·95	65·98
H_{28}	28	6·80	7·16	6·91	7·03
N_2	28	6·80	—	—	—
O_5	80	19·41	—	—	—

These numbers and the general character of the body show it to be of similar nature to those produced by the action of baryta-water on strychnine, viz., that it is a hydrobrucine, $C_{23}H_{28}N_2O_5$, formed by addition of 1 mol. of water to each molecule of the alkaloïd. This is to some extent confirmed by the action of dehydrating agents upon it. When, after dissolving in strong nitric acid and diluting, stannous chloride is added, complete decolorisation ensues; but if the alkaloïd is first dissolved in strong sulphuric acid, then nitric acid added to it, and finally stannous chloride after diluting, a faint wine-red colour is developed, whilst if the substance is heated for a few hours with the sulphuric acid, and nitric acid is then added, there is a dark reddish-brown colour, reminding one of the brucine reaction, though duller, and then on adding stannous chloride a fine wine-red colour is produced, like that obtained when brucine is itself dissolved in strong nitric acid, and diluted and mixed with stannous chloride. I was not successful in an attempt to reproduce crystalline brucine in this manner, but was only able to attempt it on a very small scale; the experiment yielded a little varnish-like substance with the above reaction. The main part of the substance was differently affected, for on addition of excess of ammonia after the treatment with sulphuric acid, a magnificent deep green coloration was produced, like that developed by exposing alkaline solutions of the original substance. This green substance was obtained as a solid by exposing alkaline mother-liquors from purifying hydrobrucine to the air, and drying *in vacuo*. It is fairly stable when dry, but less so in acid or alkaline solutions. It dyes silk and mordanted calico; the colours seem fairly permanent when dry, but will not bear much heat in presence of water.

I originally commenced these experiments hoping to obtain saponification-products, and intending to submit these to limited oxidation;

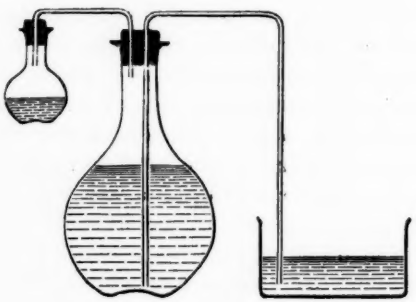
the experiments of Gal and Étard on strychnine and mine on brucine show that these alkaloïds are not affected as many others are by reagents of this kind. It will therefore be necessary to study the oxidation of these compounds in the unaltered state. This I am immediately proceeding to do; and since this paper was written, I have already made satisfactory progress in that direction.

LX.—*On the Estimation of the Value of Zinc Powder, and on a Gauge for Measuring the Volume of Gases without Calculation for Temperature and Pressure.*

By Joseph Barnes.

Having from time to time to compare samples of zinc powder, I have found that the most convenient method is to measure the amount of hydrogen liberated on treatment with an acid.

The apparatus I have adopted for this purpose is figured below:—



The smaller flask has a capacity of about 100 c.c. The larger one must hold over one litre. The syphon tube must reach the bottom of this flask. The third vessel must be sufficiently capacious to contain one litre of water, and admit the hand.

The process is as follows. One litre of water at the temperature of the room is placed in the large flask. Two grams of the zinc powder are weighed out and folded in a piece of thin paper, and dropped into the dilute sulphuric acid previously placed in the small flask. Before the acid penetrates the paper containing the zinc, there is sufficient time to connect the flask quickly with the rest of the apparatus.

The zinc powder is then rapidly attacked by the acid, and the hydro-

gen evolved forces an equivalent bulk of water out of the larger flask into the receiving vessel. When all action has ceased, the cooling of the smaller flask is hastened by surrounding it with cold water, and the whole is left undisturbed for about an hour. The hand is then placed in the receiving vessel, and whilst the water therein is at the same level as in the large flask, the syphon tube is closed by the finger. The large flask is then disconnected, and as much water from the syphon allowed to run into it as equals the original height of the litre of water in the flask. The rest of the water in the syphon may be run into the receiving vessel.

The loss of water from the litre contained in the large flask represents the volume of hydrogen evolved by the zinc powder, less the small amount dissolved by the water. If the same water be used repeatedly, the loss by solution becomes of course very small indeed.

To avoid the tedious corrections for temperature and pressure, the following kind of tension-gauge was used.

A glass bulb was drawn out at one side into a capillary tube bent at the extremity into a hook A, and on the opposite side fused to a graduated glass tube. The capacity of the bulb and value of the divisions were found by filling it with water, forcing mercury up the graduated tube, and weighing the water expelled from the bulb at A as each division was reached by the mercury. All the water was then driven out of the bulb and tube, except a small drop to keep the air saturated with vapour. It was then placed in a mercury trough made from a glass cylinder partially filled with paraffin wax (C) to economise mercury. A cork (B) fitting firmly, but not air-tight, into the mouth of the glass cylinder, and perforated to allow the graduated stem to slide easily up and down, serves to keep the gauge steady at whatever position it may be placed. The temperature and pressure of the atmosphere having been noted, the gauge was placed so that the volume of air contained in it would become 25 c.c. if dried and measured at 760 mm. and 0° C. A globule of melted wax (paraffin wax and resin) was then pressed against A, and the gauge raised a little. The wax was sucked for a very short distance into the capillary tube, where it immediately solidified. A table was made for the gauge, and instead of putting down the value of the divisions in cubic centimeters, each number was multiplied by 0·04 to convert them into fractions of unity.

To use the apparatus it is allowed to attain the same temperature

as the gas which is being measured. The bulb is then raised or lowered until the mercury inside the stem is almost on a level with that outside, due allowance being made for capillarity. The observed volume of gas is then divided by that number in the table corresponding with the division on the gauge with which the level of the inner column of mercury coincides.

The following are three results obtained in succession on three different days:—

	(1.)	(2.)	(3.)
Observed volume of moist gas.....	100·00	100·00	100·00
Corrected volume of dry gas, by calculation	94·68	90·54	91·01
Corrected volume of dry gas, by tension gauge	94·38	90·37	90·72
Difference	0·30	0·17	0·29

The apparatus is correct enough for the purpose for which it was intended, but I purpose making a more accurate one suitable for scientific purposes.

LXI.—*On the Synthesis of α-Isoheptane.*

By Thomas Purdie, B.Sc., Ph.D.

The following research, the object of which was the preparation of pure α-isoheptane, was undertaken at the suggestion of Professor Wislicenus, in order to complete a series of isomeric heptanes to be used in the determination of certain physical constants. The synthesis of this hydrocarbon has been described by several investigators, but owing to the presence of isomeric substances in the materials used, the body has never as yet been procured in the pure state. α-Isoheptane was first prepared by Wurtz in the course of his investigation of the hydrocarbons formed of the so-called mixed radicals by the action of sodium on a mixture of ethyl and amyl iodides, and it was afterwards prepared by Grimshaw and by Schorlemmer in a similar way, the corresponding bromides being used (this Journal, 1873, pp. 309, 319; *Annalen*, **166**, 163, 172). It is now well known, however, that the ordinary amyl alcohol is a mixture of several isomerides. Besides isobutyl-carbinol, it contains, according to the investigations of Erlenmeyer on the valeric acids, the optically active alcohol, so-called secondary butyl-carbinol; and it has been more recently shown by

Wischnegradsky (*Annalen*, **190**, 328) that a normal pentyl alcohol is also present.

The presence in Wurtz's ethyl-amyl of a heptane derived from secondary butyl-carbinol is indicated by its being slightly optically active, and by the fact observed by Grimshaw that the secondary heptylic alcohol obtained by chlorinising ethyl-amyl yields on oxidation a valeric acid the barium salt of which does not crystallise, a property which characterises barium methyl-ethyl-acetate obtained from the product of oxidation of the optically active amyl alcohol. The presence of a normal heptane, derived from the normal amyl alcohol above alluded to, seemed to be indicated by the physical experiments conducted by Wislicenus.

The first method of synthesis which was tried was not successful. It was thought that, according to the usual reaction between the zinc compounds of the alcohol-radicals and the alcohol iodides, the methyl group might be substituted for the atom of iodine in secondary hexyl iodide. The hexyl iodide was added to an ethereal solution of zinc methyl, and the mixture heated over the water-bath for an entire day. No reaction took place; the addition of sodium with the object of assisting the action of the zinc-methyl being also without avail. Only on heating the mixed liquids to 125° in closed tubes, did the reaction set in. On opening the tubes, large quantities of gas, apparently marsh-gas, were given off, zinc iodide and a little zinc oxide having been formed. Water having been added to the product of the reaction, the layer of oil was separated off, dried and fractionated; the oil boiled mostly at 65—66°, and proved to be chiefly hexylene. The different fractions were carefully examined for small quantities of heptane by treating with bromine and also by shaking up with sulphuric and small quantities of nitric acid. The small quantity of oil, which was not at once absorbed by the latter reagents, was gradually attacked with separation of iodine. It may therefore be concluded that by the action of zinc-methyl in ethereal solution on hexyl iodide no liquid saturated hydrocarbon is formed. As the fraction boiling almost constantly at 65—66° contained nevertheless much iodide, which seemed somewhat extraordinary, it was further examined. By treatment with sodium an inflammable gas was given off, which was not absorbed by sulphuric acid. The reaction with sodium was completed by heating in a closed tube. The remaining liquid, being distilled, was found, according to the following analysis, to be pure hexylene.

I. 0·1419 gram gave 0·1840 gram H_2O and 0·4439 gram CO_2.
II. 0·1060 gram gave 0·1387 gram H_2O and 0·3322 gram CO_2.

	Calculated for C_6H_{12}.	Found. I.	Found. II.
Carbon	85·71	85·32	85·47
Hydrogen	14·29	14·41	14·54

A combustion of the liquid, before being treated with sodium, and a determination of the iodine by the method of Carius, gave the following results:—

I. 0·2097 gram gave 0·1935 gram H_2O, and 0·4548 gram CO_2.
II. 0·2069 gram gave 0·1901 gram H_2O, and 0·4472 gram CO_2.
III. 0·5036 gram gave 0·2602 gram AgI.
IV. 0·5182 gram gave 0·2687 gram AgI.

	Found. I.	II.	III.	IV.	Mean.
Carbon	59·15	58·95	—	—	59·05
Hydrogen....	10·25	10·21	—	—	10·23
Iodine	—	—	27·92	28·02	27·97
Oxygen.....	—	—	—	—	2·75

If the iodine be calculated to ethyl iodide, the oxygen to ethyl alcohol, and the rest of the mixture calculated as hexylene, the total carbon and hydrogen amount to 58·90 and 10·38 per cent. respectively, numbers which agree closely with those found by analysis. It appears, therefore, most probable, notwithstanding the almost constant boiling point of the mixture, that the iodide present is ethyl iodide, and that by the action of zinc-methyl in ethereal solution on hexyl iodide, hydriodic acid is split off from the latter, with formation of hexylene; the hydriodic acid decomposes the zinc-methyl, zinc iodide and marsh-gas being formed, while a part of it also attacks the ether, producing ethyl iodide and ethyl alcohol.

Even the primary iodides of the higher alcohol-radicals do not react readily with the zinc compounds; thus, according to Hofmann, amyl iodide and zinc-ethyl do not react even in closed tubes. An atom of iodine, when attached to a secondary atom of carbon, is less easily replaced by a radical than when attached to the terminal carbon-atom of a chain, while at the same time it more readily splits off in combination with the hydrogen from a neighbouring carbon-atom. It is therefore not surprising that the secondary hexyl iodide should not lend itself readily to a substitution reaction. It is, however, worthy of note, that no heptane whatever was formed in the experiment described. Though the tertiary butyl iodide has been used successfully for this method of synthesis, I am not aware that the experiment has been tried before with any iodide of a secondary alcohol.

The method described having failed, the well-beaten track of the

aceto-acetic ether derivatives was resorted to. Isobutyl alcohol, unlike amyl alcohol, offers itself as an excellent material to start from, as it can be obtained free from isomerides. Isobutyl iodide was made from this alcohol in the usual way, and brought into reaction with sodium aceto-acetic ether; the isobutyl aceto-acetic ether thus obtained yielded by saponification, as chief product, a methyl isopentyl ketone, which gave by reduction a methyl-isopentyl carbinol; this was converted into the corresponding iodide, and the latter, by the action of nascent hydrogen, yielded the α-isoheptane. The products of the first five reactions enumerated were, of course, in each case isolated and approximately purified by fractional distillation. It is unnecessary to describe the various processes in detail, the synthesis having been already performed, as far as the secondary isoheptylic iodide, by W. Rohn (*Annalen*, **190**, 305), whose observations were in nearly all respects confirmed. A few alterations, which were made in Rohn's methods, and the yields obtained may, however, be noted. The isobutyl iodide was made to act on the sodium aceto-acetic ether in the way usually now followed in these syntheses (*Annalen*, **192**, 153). To effect the splitting up of the isobutyl aceto-acetic ether in the desired direction, an aqueous solution of potash was used instead of baryta-water. The ether was heated in a copper vessel, fitted with inverted condenser, over the naked flame, but at first somewhat cautiously, with twice the quantity of potash required by theory, dissolved in twice its weight of water. After three hours, the liquid was distilled off as long as oil passed over. The quantity of ketone obtained amounted to 70 per cent. of the calculated theoretical yield. The ketone yielded by reduction with sodium 72 per cent. of the calculated yield of methyl-isopentyl carbinol, boiling between 148° and 154°, and a considerable quantity of a pinacone, which is described below. The alcohol was converted into iodide by saturating it at the ordinary temperature with gaseous hydriodic acid, and then passing the gas through it while it was heated over the water-bath. The iodide, after being washed with small quantities of dilute potash-solution, and with water, was dissolved in double its volume of alcohol, poured over zinc strips, and treated with small quantities of concentrated hydrochloric acid. The action set in at the ordinary temperature with considerable evolution of heat, and was continued until hydrogen began to be given off, and the mixture was finally heated for some time. Water was then added, and the oily layer of liquid separated off. The crude product thus obtained was repeatedly shaken up with fresh quantities of sulphuric acid, and finally with sulphuric acid to which a few drops of nitric acid were added, until the oil, even after being a long time in contact with the acid, remained colourless. It was then rectified twice over sodium. The rectified oil, however, did not boil

quite constantly, and it was only after somewhat prolonged fractional distillation, that a specimen of the liquid was obtained, which boiled to the last drop between 89° and 90°, under a barometric pressure of 745 mm.; the thermometer remained during the greater part of the distillation absolutely stationary at 89·5°. The following results were obtained from analysis:—

I. 0·1071 gram gave 0·1573 gram H_2O, and 0·3299 gram CO_2.
II. 0·1050 gram gave 0·1536 gram H_2O, and 0·3239 gram CO_2.

	Calculated for C_7H_{16}.	Found. I.	Found. II.
Carbon	84·00	84·01	84·13
Hydrogen	16·00	16·32	16·25

A determination of the vapour-density was made by the Hofmann method, the details of which were as follows:—Substance employed 0·1522 gram; volume of vapour at 100° = 109·22 c.c.; height of mercury column (average temperature 95°) = 441·2 mm.; height of barometer (temperature 12°) 760·7 mm. The vapour-density at standard temperature and pressure deduced from these numbers is 3·45; theory gives 3·46.

The boiling point of α-isoheptane (89·5°) agrees closely with that of ethyl-amyl (90)°, as given by Grimshaw; Wurtz gives 88°. It is a colourless mobile liquid, having the slight and somewhat pleasant smell characteristic of the liquid paraffins. The specific gravity and other physical properties will be given by Professor Wislicenus elsewhere.

The methyl-isopentyl ketone yielded by reduction, as mentioned above, besides the secondary heptylic alcohol, a liquid which distilled with but little decomposition between 265° and 270°. Professor Wislicenus kindly placed at my disposal the high-boiling fractions obtained by him previously from the same reaction. By fractional distillation a viscous oil was obtained, which boiled at 268°, and solidified on cooling to a crystalline mass, consisting of groups of radiating needles. The substance, on being analysed, was found to be *di-isobutyl pinacone*, as appears from the following results:—

I. 0·1047 gram gave 0·1255 gram H_2O, and 0·2799 gram CO_2.
II. 0·1206 gram gave 0·1423 gram H_2O, and 0·3222 gram CO_2.

	Calculated for $C_{14}H_{30}O_2$.	Found. I.	Found. II.
Carbon	73·05	72·91	72·86
Hydrogen.....	13·04	13·32	13·11
Oxygen.....	13·91	—	—

Rohn also obtained this substance (*Annalen*, **190**, 311), not, however, in the pure state, but mixed, probably with its corresponding pinacolin. He describes it as a liquid which does not solidify at −13°. It is really a crystalline solid which melts at 30°, and then remains liquid for some time, even if subjected to low temperatures. Several attempts were made to convert the di-isobutyl pinacone into the corresponding pinacolin; but although this body was evidently formed, it was found impossible, owing to the small quantity of material available, to procure it in the pure state. By heating the pinacone with this object in view with dilute sulphuric acid (one of acid to one of water), an oil was obtained which, after being dried with potassium carbonate, distilled about 230°, and did not solidify. The liquid remained slightly yellow, and gave on analysis numbers for the carbon about 3 per cent. higher than that calculated for the formula $C_{14}H_{28}O$. By treatment with acetyl chloride, the pinacone yields apparently the same oil, but contaminated with traces of a chlorine compound, from which no doubt it could be freed, were a sufficiently large quantity of the substance available to admit of fractional distillation.

I beg, in conclusion, to thank Professor Wislicenus, in whose laboratory the work was done, for the help he kindly gave me during the prosecution of the research.

LXII.—CONTRIBUTIONS FROM THE LABORATORY OF THE ROYAL COLLEGE OF CHEMISTRY.

On a New Derivative of Quinine.

By Edward H. Rennie, M.A. (Sydney), B.Sc. (London).

It is stated in *Watts' Dictionary of Chemistry* (vol. **5**, p. 18), that quinine dissolves in cold concentrated nitric acid without coloration (Riegel), and without forming picric acid (Liebig), but beyond this the action does not seem to have been investigated.

The experiments recorded below were undertaken to ascertain the action of a mixture of concentrated nitric and sulphuric acids upon quinine.

If quinine hydrate be added in large quantity to a mixture of the strong acids, the liquid speedily becomes warm, and a violent reaction sets in, with copious evolution of red fumes. If, on the other hand, the alkaloïd be added in small quantities at a time, the liquid at the

same time being kept cool, it dissolves with little or no evolution of gas, forming a reddish-yellow liquid. As it seemed possible that in the latter case a nitro-derivative might be formed, a considerable quantity of quinine hydrate was dissolved in a mixture of equal volumes of pure concentrated sulphuric and nitric acids, as above described, the whole allowed to stand for a time, then largely diluted with water, and ammonia added in excess. A bulky brownish-yellow amorphous precipitate was immediately thrown down. A preliminary examination having shown that this substance does not possess the properties of ordinary quinine, the bulk of the precipitate was collected on a filter, then well washed with water, and finally shaken up and washed with ether to remove any unaltered quinine. It was then dried, first over sulphuric acid, and finally at 100°.

All attempts to crystallise the substance thus prepared proved futile. It is easily soluble in alcohol, scarcely soluble in water or ether. It dissolves easily in acids, but does not form crystallisable salts. Its solution in hydrochloric acid gives with platinic chloride a brownish-yellow precipitate, which, however, appears to be very unstable. It does not give the quinine reaction with chlorine-water and ammonia. Heated over 200° it decomposes suddenly, evolving large quantities of gas.

The analyses of two separately prepared specimens dried at 100° gave the following results :—

A.	0·1074 gram substance yielded ..	0·0554 H_2O.
	„ „ „ ..	0·2195 CO_2.
	0·1160 gram substance yielded ..	0·0616 H_2O.
	„ „ „ ..	0·2370 CO_2.
B.	0·1036 gram substance yielded ..	0·0550 H_2O.
	„ „ „ ..	0·2122 CO_2.

Two nitrogen determinations of specimen A gave 13·12 and 13·52 per cent. of nitrogen. Further examination showed that heating to 100° does not drive off the whole of the water, but that a temperature of from 120—130° is necessary to that end.

Water determinations were therefore made by heating the steam-dried substance to 120—130° in an air-bath, till constant in weight, with the following results :—

A. 0·2238 gram lost 0·0096 gram = 4·29 per cent.
B. 0·5751 gram lost 0·0250 gram = 4·34 per cent.

On comparing together the above numbers, it appears that they agree fairly well with those required for a dinitroquinine monohydrate, $C_{20}H_{22}(NO_2)_2N_2O_2,H_2O$.

		Found.		
		A.		B.
	Theory.			
C.....	55·55	55·74	55·77	55·86
H	5·55	5·73	5·90	5·89
N	12·97	13·12	13·52	—
H_2O ..	4·20	4·29		4·34

Analyses of different specimens of the platinum salt gave very unsatisfactory results. In fact it was evident that this, like other salts of the base, is very unstable, being decomposed more or less in the processes of washing and drying.

The uncrystallisable nature of the substance and its salts, and the consequent uncertainty as to the purity of the product obtained, of course render the conclusions to be drawn more or less doubtful; but the general behaviour of the body points clearly to a nitro-derivative, while the fairly close agreement of the numbers obtained with the theory, coupled with the fact that a nitro-group more or less would make a difference of 5 or 6 per cent. in the proportion of carbon, renders it at least probable that the base is really a dinitroquinine.

Attempts to prepare a corresponding *amido*-compound have hitherto proved unsuccessful.

LXIII.—*On the Synthetical Production of Urea from Benzene, Ammonia, and Air, by the Action of Heated Platinum.*

By E. F. Herroun, Daniell Scholar of King's College, London.

In conducting some experiments with a coil of platinum wire, heated to a bright redness, it was observed that on placing this coil in a flask containing a small quantity of benzene and ammonia solution, the flask in a short time became coated with a white deposit.

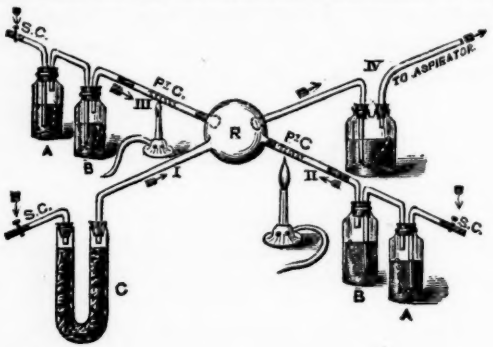
As, however, the quantity of substance produced by this means was too small for the purposes of analysis, the following alteration in the mode of its formation was made:—

Air was drawn, by means of an aspirator, through washing bottles containing (1) ammonia and (2) benzene, the glass tubes conveying the air dipping below the surface of the liquid in both bottles, then through a tube containing a helix of platinum wire, heated to dull redness by a Bunsen burner, and finally through water, contained in potash bulbs, to absorb the products of the action.

On analysis the water, at the end of the experiment, was found to contain ammonium carbonate, nitrite, and nitrate; but it was also observed that a solid crystalline substance had collected in the tube containing the platinum, depositing not far from the heated wire. On analysing this substance qualitatively it appeared to be ammonium cyanate, giving the following reactions:—When treated with dilute sulphuric or hydrochloric acid it evolved cyanic acid, recognised by its odour; its solution gave with silver nitrate a white precipitate, soluble in dilute nitric acid, and converted by hydrochloric acid into silver chloride, with evolution of cyanic acid. After boiling its aqueous solution and evaporating to a small bulk, it gave with strong nitric acid a crystalline precipitate, soluble in potash solution, and evolving ammonia when boiled with it, indicating its conversion into urea.

In order to obtain as large a quantity of the substance as possible, I adopted the form of apparatus shown in the diagram, in which two tubes containing heated platinum are used, and the product formed is allowed to collect in a bulb (diagram).

Apparatus for the Synthetical Production of Urea.



Air enters the globular receiver R, by the tubes II and III impregnated with ammonia and benzene vapour by bubbling through the bottles AA and BB, containing strong ammonia-solution and benzene respectively; the proportion of air that is admitted is regulated by the screw-clips S.C. S.C. Before entering R the air, ammonia, and benzene-vapour pass through the coils of platinum wire PtC PtC, which are heated by the Bunsen burners.

The tube I delivers air, dried by passing through the tube C, containing dried calcium chloride. This dry air removes the excess of ammonia and most of the ammonium carbonate and water.

When this form of apparatus is employed, the ammonium cyanate first produced is entirely converted into urea. The maximum product is obtained when a slow current of air is passed through the ammonia

and benzene, because if much air is used, the benzene appears to be entirely converted into carbon dioxide and water.

The urea thus formed was found not to be pure, but mixed with ammonium carbonate and sulphate (derived from carbon disulphide in the benzene), and with an organic impurity apparently of a resinous nature, the presence of which, it is curious to observe, prevented the precipitation of urea by oxalic acid. This impurity is soluble in ether. To purify the urea, the solution which collects in the bulb was evaporated to dryness, the residue extracted with absolute alcohol, filtered, evaporated to a small bulk, and the urea precipitated by excess of ether. It was found necessary to repeat this process, or to recrystallise from alcohol several times in order to obtain the urea sufficiently pure for organic analysis. In performing the analysis of the substance, the carbon and hydrogen were determined in the usual way by combustion with oxide of copper.

The nitrogen was determined by conversion into ammonia by heating with soda-lime, the ammonia being absorbed by hydrochloric acid, and precipitated by excess of platinic chloride, and the precipitate was washed, dried, ignited, and weighed as metallic platinum.

The following table gives the results of the carbon and hydrogen determinations:—

Amount of substance taken.	Weight of CO_2 found.	Percentage of carbon.	Weight of H_2O found.	Percentage of hydrogen.
1. 0·1746 gram	0·133 gram	20·73	0·109 gram	6·93
2. 0·185 „	0·142 „	20·9	0·115 „	6·86
3. 0·292 „	0·2155 „	20·14	0·18 „	6·84

The determination 3 was obtained from a sample of urea which was quite white, while the two determinations 1 and 2 were obtained from samples which were coloured yellow by the resinous impurity before mentioned; and since urea contains less carbon than almost any common organic bodies, the presence of a small amount of foreign organic matter would account for the high percentages of the two first determinations.

The following table gives the results of the nitrogen determinations:—

Weight of substance taken.	Weight of Pt obtained.	Corresponding percentage of N.
0·1568 gram	0·514 gram	46·5
0·298 „	0·976 „	46·51
0·192 „	0·630 „	46·6
0·171 „	0·564 „	46·83
0·203 „	0·6645 „	46·48

The following numbers give the mean of the whole results:—

	Mean. Found.	Calculated.
Carbon.....	20·88 per cent.	20·00 per cent.
Hydrogen	6·87 „	6·66 „
Nitrogen.....	46·584 „	46·66 „
Oxygen (by diff.) ..	25·666 „	26·66 „
Total	100·00 „	99·98 „

The substance produced answers all the characteristic tests for urea, that is (1), on boiling with potash it gave ammonia. (2) On treating it with nitric acid, crystals of urea nitrate separated. (3) Oxalic acid produced crystals of urea oxalate after the resinous impurity had been removed by washing with ether. This fact, together with the determinations above given, leaves no doubt as to its identity. The numbers obtained by the analysis of the perfectly colourless sample give the following percentage composition:—

	Found.	Required.
Carbon	20·14	20·00
Hydrogen	6·84	6·66
Nitrogen.....	46·60	46·66
Oxygen	26·42	26·66

As it seemed probable that other substances besides the heated platinum wire might yield larger quantities of the substance, the following experiments were tried:—

Heated spongy platinum and platinised asbestos were tried as substitutes for the platinum wire, but they apparently produced too much oxidation, forming more ammonium carbonate and less urea, than in the case of the wire.

Platinised charcoal produced small quantities of urea, but it acts slowly and requires a high temperature, probably owing to the reducing action of the charcoal.

Olefiant gas was also employed in some experiments instead of benzene, when it was found that large quantities of ammonium carbonate were produced, but no urea.

From the relationship existing between them it was determined to substitute acetylene for benzene, and it was found that in this case a considerable amount of urea was produced, the acetylene behaving in a manner very similar to the benzene vapour.

Further experiments with regard to this last mode of formation of the urea are now in progress.

LXIV.—*The Effects of the Growth of Plants on the amount of Matter removed from the Soil by Rain.*

By E. W. Prevost, Ph.D.

In a paper which I read last year before the Society, I gave an account of experiments which showed the influence exerted by the growth of plants in a soil on the drainage-water from that soil. In those experiments the composition of the water which flowed from soil 4 inches deep, and in which clover was growing, was found to be greatly different from that which flowed from the same soil, but in which there was no vegetation. The amount of solids removed was 12·5 grams (48 grains per gallon) from "clover soil," and 50 grams (220 grains per gallon) from the "blank."

During the past season I have repeated the experiments, but using in the place of shallow pans large glazed stoneware pans, 18 inches broad, with perpendicular sides 10 inches high, and provided with a hole at the bottom, from which the drainage-water flowing was collected in jars placed below.

In these pans were placed 100 lbs. of soil, which, when beaten down, filled the pans up to 1 inch of the top, leaving a clear 9 inches for the growth of the plants. The following is an analysis of the soil:—

Moisture	5·06 per cent.	
Calculated on the dry soil—		
Soluble salts (containing sulphates and traces of chlorides)	0·680	,,
Organic matter	11·80	,,
(Containing nitrogen equal to ammonia	0·436)	,,
SiO_2	24·54	,,
P_2O_5	1·185	,,
$CaCO_3$	53·98	,,
Al_2O_3	3·065	,,
Fe_2O_3	3·84	,,
MgO	0·58	,,
K_2O	0·451	,,
	99·441	

Owing to the delay experienced in obtaining the kind of pan which I desired, I decided to repeat the same experiments as last year in

shallow pans, holding only 28 lbs. of soil (depth of soil 4 inches), which had been coarsely sifted: therefore on May 4th I sowed in No. I clover seeds, and No. II was left "blank."

It was not until late in the season that I was able to sow seeds in the large pans, but on June 18th there was sown in No. 3 cabbage seed; in No. 4, wheat; in No. 5, beans; in No. 6, "cow-grass" (common perennial clover); in No. 7, garden turnips; and No. 8 was left blank. All the pans were placed in a moderately sheltered spot, and surrounded by a spacious wire cage, so as to exclude birds, leaves, &c.

As the season was favourable, the plants flourished up to the date when it was considered necessary to discontinue the experiment, and, with the exception of the wheat and turnips, all reached maturity, and the growth of the clover had been strong enough to allow of a crop being taken off.

When it appeared that the plants were suffering from drought, equal quantities of distilled water were poured upon them evenly, and this water amounted altogether to 2 gallons (9 litres). The drainage-water which had collected in the jars below the pans, and had been from time to time evaporated in basins nearly to dryness, amounted in the case of No. I, to 20·26 litres; No. II, to 24·54; No. 3, to 10·91; No. 4, to 14·90; No. 5, to 11·97; No. 6, to 9·12; No. 7, to 18·95; No. 8, to 14·95. The plants were wholly removed from the soil on September 21st, and during the interval, May 4—September 21, 16·2 inches of rain = 14·87 gallons, and during the interval, June 18—September 21, 14·7 inches of rain = 13·529 gallons had fallen; to this quantity the 2 gallons of distilled water must be added, making therefore a total "rainfall" of 18·38 inches (16·87 gallons = 76·45 litres), and 16·88 inches (15·529 gallons = 70·56 litres) respectively.

The drainage-water when evaporated yielded, in each case, of solid matter:—I, 7·092 grams; II, 25·576; (3), 5·039; (4), 6·463; (5), 6·942; (6), 5·422; (7), 7·024; (8), 12·862.

The plants, after careful cleansing so as to remove as far as possible all adhering soil, which was found to be most difficult, as the fine fibres persistently retained a certain portion of soil, yielded on ignition the following amount of ash:—

I = 21·32 grams; 3 = 3·53; 4 = 8·05; 5 = 10·42; 6 = 18·503; 7 = 3·69.

During the evaporation of the water, a small amount of organic matter separated out, and this being different in each case, as regards quantity and colour, affected the appearance of the dry residues, which were of varying shades of pale reddish-brown, and very deliquescent.

The following Table I shows the amount of solid matter removed from each sample of soil by the drainage-water, the total ash of the

crops, &c. In the fourth column will also be found the amount of solid matter removed per gallon of drainage-water, the mean quantity obtained from 3, 4, 5, 6, and 7 being 34 grains per gallon, a quantity not widely differing from that obtained by Völcker in 1866—69, viz.,

TABLE I.

Plants.	Drainage-water, in litres.	Solid matter in drainage-water, in grams.	Solid matter in drainage-water, in grains per gallon.	Total dry matter of crop, in grams.	Total ash in crop, in grams.	Total solids removed from soil by drainage-water and crop, in grams.	Development of crop.
I. Clover .	20·26	7·092	24·500	121·90	21·32	28·412	Very strong.
II. Blank .	24·54	25·576	73·11	—	—	25·576	—
3. Cabbage	10·91	5·039	32·39	30·64	3·53	8·569	Poor.
4. Wheat .	14·90	6·463	30·43	41·86	8·05	14·513	Strong and healthy, blossom barely reached.
5. Beans ..	11·97	6·942	40·68	138·24	10·42	17·364	Very healthy strong pods, well formed.
6. Clover..	9·12	5·422	41·703	134·37	18·503	23·925	Very strong and healthy.
7. Turnips	18·95	7·024	26·00	22·01	3·69	10·714	Poor, leaves healthy and developed, bulbs not so.
8. Blank..	14·95	12·862	60·451	—	—	12·862	—

33·3 grains per gallon, from unmanured fields in which wheat was growing. Table II shows the amount of all the constituents present in the drainage-waters in grains per gallon, and the percentage composition of the total solids removed by the water from the soil; and in III will be found the absolute quantities of each of the several constituents.

TABLE II.

	No. I. Clover.		No. II. Blank.		No. 3. Cabbage.		No. 4. Wheat.	
	Per cent. of solid matter.	Grains per gallon.	Per cent. of solid matter.	Grains per gallon.	Per cent. of solid matter.	Grains per gallon.	Per cent. of solid matter.	Grains per gallon.
Loss on ignition	26·06	6·384	15·82	11·566	13·89	44·990	13·91	4·233
SiO_2	7·02	1·719	2·93	2·142	10·85	3·514	3·68	1·119
Cl	3·93	0·9628	6·08	4·445	0·52	0·1694	0·57	0·1734
SO_3.....	13·45	3·295	18·56	13·569	7·90	2·558	14·50	4·412
CO_2	16·50	4·0425	0·96	0·7018	19·46	6·3028	20·40	6·207
P_2O_5	2·85	0·702	2·78	2·0324	3·05	0·988	1·19	0·3621
Al_2O_3.....	3·45	0·7962	1·67	1·2209	4·64	1·725	1·88	0·5721
Fe_2O_3.....	0·96	0·2362	0·58	0·424	0·51	0·1502	0·30	0·9129
CaO	30·13	7·3778	12·84	9·387	34·50	11·430	36·02	10·961
MgO	2·37	0·5806	2·62	1·184	3·15	1·0203	4·23	1·287
K_2O	1·82	0·4459	6·64	4·8544	5·24	1·697	3·76	1·144
Na_2O	6·97	1·6076	15·02	10·981	6·07	1·966	3·08	0·937
NH_4	0·83	2·4426	2·08	1·5206	1·10	0·3562	0·48	0·1476
N_2O_5	9·97	0·2073	28·06	20·5147	1·54	0·4998	7·24	2·200

	No. 5. Beans.		No. 6. Clover.		No. 7. Turnips.		No. 8. Blank.		Average percentage composition of solid matter in drainage from 3, 4, 5, 6, 7.
	Per cent. of solid matter.	Grains per gallon.	Per cent. of solid matter.	Grains per gallon.	Per cent. of solid matter.	Grains per gallon.	Per cent. of solid matter.	Grains per gallon.	
Loss on ignition	6·72	2·745	19·80	8·257	11·03	2·868	16·93	10·234	13·07
SiO_2	1·94	0·7926	4·36	1·818	10·59	2·7534	6·82	4·123	6·28
Cl	0·90	0·3677	1·74	0·7356	0·15	0·039	0·85	0·5138	0·77
SO_3.....	10·43	4·262	9·07	4·672	14·31	3·6206	11·14	6·7342	11·24
CO_2.....	22·10	9·0902	14·28	5·945	14·53	3·7778	7·84	5·0394	18·15
P_2O_5	0·73	0·298	1·15	0·4796	2·16	0·5616	1·70	1·0276	1·65
Al_2O_3	0·07	0·0286	0·51	0·2127	3·32	0·8632	2·77	1·6745	2·08
Fe_2O_3	trace	trace	0·43	0·179	0·58	0·1508	0·34	0·2055	0·36
CaO	30·36	12·406	26·75	11·155	24·48	6·365	26·83	16·418	30·42
MgO	1·18	0·482	3·32	1·384	3·54	0·9204	3·15	1·9042	3·12
K_2O	4·60	1·871	4·38	1·8266	4·18	1·0868	5·96	3·6029	4·43
Na_2O	2·32	0·9479	2·70	1·126	3·00	0·7800	2·66	1·6080	3·43
NH_4	0·89	0·3579	0·93	0·3868	0·55	0·143	0·34	0·2055	0·79
N_2O_5	1·60	0·6468	24·35	10·1546	2·50	0·533	24·87	15·034	7·44

From the figures in Table II it will be seen that all the crops prevented relatively the removal of a considerable quantity of soluble material; and not only relatively was this removal prevented, but also absolutely, as reference to Table I shows, in which it appears that the solids removed from "blank" are nearly double in weight of those removed from some of the pans, viz., 12·8 and 7 grams, and at the same time, with one exception, the percolation was the highest.

Comparison of the *weight* of the ash of the crops with that of the solids removed by drainage appears to indicate that those plants which remove most material in their ash, also cause a large amount of matter to become soluble in the soil (in addition to what they are capable of absorbing), and in consequence to be lost:—

	Turnips.	Beans.	Wheat.	Clover.	Cabbage.
Soluble matter in drainage-water, grams....	7·024	6·942	6·463	5·422	5·039
Ash of crop, grams....	3·690	10·420	8·050	18·500	3·530
Percentage of ash in plants	16·800	7·550	19·250	13·770	11·520

Clover and turnips are an exception to this statement, which is founded on the slenderest basis, and is consequently untrustworthy; for not only is the number of experiments insufficient for the foundation of such a theory, but also the separation of adhering soil, as before stated, was most difficult; and more especially was this found to be the case when preparing the wheat plants for analysis, the rootlets having ramified through the whole soil, rendered the percentage of ash very high, 19 per cent. (containing 56 per cent. SiO_2).

There was much less difficulty experienced in freeing the roots of the other plants from soil, therefore I believe that the figures representing the total ash of these plants are approximately correct, whereas the ash of the "wheat" should be much lower.

Comparison of Tables III and IV does not show any definite relationship to exist between the composition of the substances removed by drainage and by the plants; still, taking into consideration only the most important ash-constituents, it is possible that we here have indications (though quite as slight as those above referred to) of some relationship between the loss experienced by the soil through drainage, and the loss due to the plants. When a plant removes much of a certain substance, that substance appears in smaller quantities in the drainage, and this is what is to be expected. Seeing, however, that this statement is contradictory to the former one made concerning the weight of the total solids in the drainage-waters, it should be pointed

TABLE III.—*Absolute Quantities removed by Water from Soil (in grams) calculated from Tables I and II.*

	I. Clover.	II. Blank.	3. Cabbage.	4. Wheat.	5. Beans.	6. Clover.	7. Turnips.	8. Blank.
Loss on ignition	1·8481	4·0461	0·6999	0·8990	0·4665	1·0735	0·7747	2·1775
SiO_2	0·498	0·7493	0·5468	0·2378	0·13467	0·2364	0·7403	0·8862
Cl	0·2787	1·5550	0·0262	0·0368	0·0625	0·0943	0·01053	0·1123
SO_3	0·9539	4·7469	0·3981	0·0937	0·7240	0·4917	1·0051	1·4328
CO_2	1·1702	0·2455	0·9807	1·3184	1·5341	0·7742	1·0206	1·008
P_2O_5	0·2021	0·7110	0·15369	0·0668	0·05067	0·06225	0·1517	0·2186
Al_2O_3	0·2446	0·4271	0·2338	0·1215	0·00486	0·0276	0·2332	0·3563
Fe_2O_3	0·0681	0·1483	0·0257	0·0194	trace	0·0233	0·0407	0·0437
CaO	2·1368	3·2839	1·7384	2·3279	2·1076	1·4508	1·7195	3·4503
MgO	0·1681	0·6702	0·1587	0·2146	0·0819	0·1800	0·2486	0·4050
K_2O	0·1291	1·6982	0·2141	0·2831	0·3193	0·2375	0·2936	0·7664
Na_2O	0·4953	4·8415	0·3058	0·1991	0·1610	0·0146	0·2107	0·3421
NH_4	0·0588	0·5319	0·0554	0·0601	0·0619	0·0542	0·0386	0·0437
N_2O_5	0·7071	7·1766	0·0786	0·4679	0·1110	1·3202	0·1756	3·1987

out that the increase of some of these solids is probably due to the root-action, producing carbon dioxide in larger quantities, and to the greater amount of nitrification which has apparently taken place in some cases than in others. Further experiments are therefore required to determine whether the solvent action produced by carbon dioxide and by nitrification preponderates over the absorption by the plant of the soluble material produced, or whether the opposite is the case. But as regards the nitric acid in the water, the case seems to be reversed, for we find that from those soils on which the more nitrogenous plants were growing, a greater amount of nitric acid passed away in the drainage.*

TABLE IV.—*Amount of principal Ash-Constituents removed by Plants (in grams.)*

	3. Cabbage.	4. Wheat.	5. Beans.	6. Clover.	7. Turnips.
SiO_2	0·1107	4·5112	0·4231	1·1749	0·0952
P_2O_5	0·4977	0·41377	0·8086	1·5700	0·5088
CaO	0·3671	0·4508	0·9419	3·7006	0·0786
MgO.....	0·0604	0·4395	0·2136	0·5292	0·1144
K_2O	0·9263	1·1068	3·4050	4·4388	0·9882

As might be expected, potash and phosphoric acid are not eliminated in the same quantities as from the "blank," and nitric acid, a most essential plant-food, is comparatively speaking removed in but small quantities when plants are growing; this is, however, not found to be the case with "clover," for there we find about half as much nitric acid appearing as from the "blank;" this peculiarity is not shared to such an extent by the drainage-waters from the shallow pans I and II, but reference to last year's experiments shows that the residues from "clover" drainage contained 1·65 grams, and those from the "blank" 6·65 grams N_2O_5. We may therefore assume that although clover assimilates a large quantity of nitrogen, yet the influence of its growth is to cause the oxidation of a considerable amount of nitrogen in the

* Owing to circumstances which have prevented the full carrying out of the analysis as I had wished, I am unable to give the remaining ash-constituents and the nitrogenous matter present in the plants; being able to employ only approximate figures representing the composition of the whole plant, I prefer only to arrange the plants firstly in order of their richness in albuminoïds, commencing with the maximum, and to compare this order with that in which they are arranged according to the nitric acid in the drainage-waters. In the first order will stand clover, beans, wheat, turnips, cabbage; in the second, clover, wheat, turnips, beans, cabbage. It will be seen that "beans" form the only exception, the others falling into their respective places.

soil, which nitrogen is not retained. This excess of soluble nitrogen may be due, as Dr. Völcker has suggested, to the continuous decay of parts of the plant, the dead parts which fall on the soil, yielding up their nitrogen to that soil, and Dr. Völcker has shown that a larger supply of soluble nitrogen is produced in the soil when a clover crop has been cut and allowed to grow again, than when the crop remains in the soil without cutting. It will be remembered that a crop was taken off the "clover."

That some of the drainage-waters should be richer in carbonates when plants are growing, is scarcely a cause for wonder, and must be due to the elimination of carbon dioxide by the roots of the plant, and is probably dependent *to some extent* on the root surface. The wheat possessed, as far as could be judged without actual measurement, the largest root surface, and we find that from the soil in which it grew there was removed (with the exception of "beans") the maximum amount of carbonates. It will also be found on reference to II that the percentage of carbonates present in the dry residues is far higher when plants are growing than when the soil is bare.

I might also point out the fact that sulphates are present in greater proportion in the water which passed from beans, clover, and turnips, and these are the crops which are supposed to require sulphates for their better development.

Potash, as before mentioned, is retained to a certain extent, and if the soil had been deeper the quantity eliminated would most likely have been considerably reduced. The same reason will account for the large amount of ammonium compounds (*vide* Table III, pan II, and in 1880 "blank" yielded 1·45 grams); but that there should be a larger quantity passing away when the soil supports life than when there is nothing growing in the soil (*see* 3, 4, 5, and 6), I cannot as yet explain. Possibly it is due to the non-retention of potash, for an increase in potash seems to be accompanied by an increase in ammonia; now it is known that the addition of a solution of potassium salts causes the removal of ammonia compounds from a soil, and in the cases in question we have an excess of potassium compounds passing over soil containing ammonium compounds, and therefore ammonium compounds should be eliminated; and we do find that, speaking generally, the larger quantities of potash are accompanied by an increase of ammonia; but against this there appears the "blank" plot, with *maximum* potash and *minimum* ammonia, but I and II are not an exception; likewise in 1880 from the "blank" there passed 1·35 grams NH_4 and 4·5 grams K_2O, while from the "clover" 0·031 gram NH_4 and 1·2 grams K_2O.

Percolation.—The quantity of water which passed through the experimental soils was, as has been stated (Table I), very varying, and

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as the depth of the soil was much less than the shallowest employed by Messrs. Lawes and Gilbert (20 inches) no satisfactory comparisons can be drawn between the two sets of experiments. Messrs. Lawes and Gilbert found, during the months June to September, that the percolation was 19·7 of the rainfall (*Inst. Civ. Eng.*, **14**); during the same period my uncropped soil gave percolation 21·2 per cent. of rainfall.

	I.	II.	3.	4.	5.	6.	7.	8.
Percentage of percolation to rainfall	26·5	32·1	15·3	21·1	14·1	12·9	26·8	21·2

This figure, 21·2, is below that given by Mr. Greaves (28 per cent.) and above that given by M. Gasparin (20 per cent.);* but seeing that the soils were all of various depths and kinds, that 28 per cent. and 20 per cent. are derived from the observations extending over twelve months, and not over only four, no satisfactory conclusion can be arrived at. Marié-Davy appears to have ascertained the percolation through soils when covered with different kinds of vegetation, but I have not as yet been able to compare his results with mine, and I have therefore introduced the above table of percolation for future comparison.

I would, however, call attention to the "turnips" and "beans," where we find with the same rainfall of 16·88 inches (15·529 gallons) that there is a very marked difference between the percolation through one soil and through the other, viz., 26·8 per cent. and 14·1 per cent. of the rainfall; in both cases there were only half-a-dozen plants growing, and both presenting apparently a considerable leaf-surface; and whereas that of the turnips afforded considerable shelter to the soil beneath, that of the beans afforded but little, as these latter plants grew high and strong. Now percolation is dependent on evaporation, and an increase of vegetation causes diminution of percolation. The large amount of dry matter in the beans (138 grams) is the result of vigorous growth, which has diminished the passage of water through the soil to a much greater extent than in the case of the turnips, whose dry matter amounted only to 20 grains. Clover (No. 6), with a smaller amount of dry matter (22·01 grams), seems to have allowed less percolation than any other plant (viz., 12·9 per cent. rainfall); but I think that this must be due to the fact that, as the crop was very thick and strong, the whole of the rain did not reach the soil, but remained in the leaves and evaporated.

Little need be said concerning plots I and II, as the depth of the soil was manifestly insufficient to allow of any conclusions, however

* The figures quoted from MM. Greaves and A. Gasparin are for 12 months, and not for June to September only.

indefinite, being drawn from the amount of water percolating through; in fact I introduced these two merely to supplement last year's experiments, and have found that they, on the whole, corroborate the results then obtained, however incorrect they may be.

Differing vastly as the plants do in their effects on the soil, the figures in Table II representing the percentage composition of the solid matter removed by drainage, show that the mean of all these influences, as measured by the composition of the residues, is very similar to those produced by the slow action of air and rain alone. Still, seeing that the absolute amount of soluble matter removed and lost when no plants are growing, is so much greater than during the growth of a crop, it evidently is far better to allow some crop to remain on the land than to leave it lying absolutely fallow. The experiments also show why a deep soil is more fitted for growth than a shallow soil, more especially in regard to the nitric acid. I hope at some future time to repeat these experiments in a more extended form, and in pans of a different shape, which shall prevent all chances of the water passing down between the sides and the soil, and trust, after a sufficient number of seasons, to arrive at some definite results. In conclusion, I must return my hearty thanks to my assistant, Mr. C. Rawson, F.C.S., for the care with which he has performed the various analyses connected with this work.

LXV.—*Metallic Compounds containing Bivalent Hydrocarbon Radicles.* Part II.

By J. Sakurai, F.C.S.

In a former communication (*Chem. Soc. J.*, 1880, Trans., 658) an account was given of a new organo-mercury compound, of which the interesting feature was the bivalent character of the hydrocarbon radicle contained in it, viz., methylene; this being, so far as I can ascertain, the first body ever obtained of its class. The bivalent function of the organic radicle, as well as of the metal, naturally suggests the existence of a second compound similar to the first, but containing an additional atom of mercury. Thus—

(1.) $I(CH_2)HgI$.
(2.) $IHg(CH_2)HgI$.

This second compound, which is related to methylene iodide in the same way as mercuric iodomethide, (CH_3HgI), is to methyl iodide,

can be easily obtained by exposing a mixture of methylene iodide with an excess of mercury to the action of light. It is desirable to add a little mercuric iodide, so as to form mercurous iodide, which keeps the metal in a finely divided state, and facilitates the reaction. Mercurous iodide also acts chemically by liberating mercury and reproducing mercuric iodide, as explained in the paper already referred to.

On a bright sunny day the reaction shows itself abundantly in a few minutes, and the mixture gets so thick that it becomes necessary to add some liquid so as to render it sufficiently fluid. Ether is most convenient for this purpose. The reaction may be carried on either in a sealed tube or in a well-corked bottle, which must be constantly shaken so as to expose as much fresh surface as possible to the action of light. The reaction takes from one to several days, according to the state of the weather and the frequency of shaking. If the mixture has been left for a sufficient length of time with constant shaking, the whole of the methylene iodide will be converted into the di-mercury compound; if not, a small quantity of mono-mercury methylene iodide will generally be found unconverted.

In order to get the di-mercury methylene iodide in a state of purity, the following plan was adopted:—

The tube or the bottle is opened, and its contents transferred to a flask. The ether is distilled off, and the residue is well digested with a strong solution of potassic iodide, which dissolves out mercuric iodide, and decomposes any of the mercurous iodide. It is first washed with an aqueous solution of potassic iodide and then with water, till it is free from mercuric iodide and potassic iodide, and afterwards dried. In order to purify it from mercury and mono-mercury compound, the whole is dissolved in hot methylene iodide, whereupon any excess of the metal collects at the bottom of the flask or beaker into a globule. The clear liquid is either decanted or passed through a hot filter. Crystals are rapidly deposited on cooling, the first portions consisting of pure di-mercury compound, whilst later crops and the mother-liquor contain the mono-mercury compound. The first crops are drained, washed with methylene iodide, and then thoroughly with ether, till a drop of the washing rapidly evaporates without leaving any oily residue.

Di-mercury methylene iodide thus obtained is a yellowish crystalline powder, insoluble in all the ordinary solvents, soluble only in hot methylene iodide. Even in that liquid it dissolves to a much less extent than the mono-mercury compound, and only on heating. It melts somewhere about 230° C. with partial decomposition. The method employed for ascertaining its composition is exactly the same as that described in the previous paper, viz., heating it in a sealed tube with a known quantity of pure iodine, ascertaining how much iodine has

been taken up, and determining the quantity of mercury obtained from it. Mercuric iodide and methylene iodide were, as before, the only products of the reaction—

$$IHgCH_2HgI + 2I_2 = 2HgI_2 + CH_2I_2.$$

Analytical results are shown below:—

	I.	II.
Substance taken.....	0·58000	0·4230
Pure iodine taken	0·55600	0·4731
„ „ left	0·11592	0·1513
„ „ used up	0·44008	0·3218
Also mercuric sulphide	0·40600	0·2939

These data give the following numbers per cent.:—

	I.	II.	Calc. for $CH_2Hg_2I_2$.
Iodine used up.....	75·88	76·08	76·05
Mercury	60·34	59·91	59·88

The same compound may also be obtained from the mono-mercury compound, (CH_2HgI_2), by simply mixing the latter with some mercury, and exposing the mixture to the action of light. It is desirable, as before, to add some mercuric iodide and ether, and the tube or the bottle must be frequently shaken. The product is purified in exactly the same manner as before.

On heating di-mercury methylene iodide with an aqueous solution of potassic iodide or with dilute hydrochloric acid, it yields mercuric iodomethide, which may be sublimed up along the neck of the flask—

$$IHgCH_2HgI + HCl = IHgCH_3 + Hg\begin{cases} I \\ Cl. \end{cases}$$

The same product seems also to be formed by heating the compound with ethyl bromide or iodide to about 140° in a sealed tube. When ethyl bromide or iodide which has been so treated, is shaken up with a strong solution of potassic iodide, and gently distilled over a water-bath, some crystalline product is left behind, soluble in ether, alcohol, ethyl bromide, or ethyl iodide, and crystallisable therefrom in thin shining plates, which have the characteristic odour of mercuric iodomethide or iodoethide, and melt at 143°, corresponding therefore with the melting point of the former of these compounds.

How that body is formed is difficult to understand. What had been expected to be formed was mercuric iodo-propide, thus—

$$IHgCH_2HgI + C_2H_5I = IHgC_3H_7 + HgI_2.$$

The investigation is still being continued in this direction, with the view of building up propyl-compounds from those of ethyl.

In the previous communication it was stated that a body insoluble even in hot methylene iodide is formed, together with mono-mercury methylene iodide, and that this body was supposed to be $CH_2Hg_2I_2$. The existence of a body having that formula, and *soluble* in hot methylene iodide being fully established by the experiments above described, a question arose as to what this insoluble body could be. That it may be an isomeride, having the constitution—

$$I(CH_2)—Hg—HgI,$$

was highly improbable, on account of its great stability, even boiling hydric chloride failing to separate metallic mercury from it. Pains were therefore taken to get the body in as pure a condition as possible, and on a careful examination it was found that the product formed by the action of iodine upon it was not methylene iodide, but iodoform. The numerical results of the analysis remained, however, nearly the same as before, *i.e.*, as for $CH_2Hg_2I_2$. This is exactly what it ought to be, if the insoluble body has the formula $CHHg_3I_3$—a new organo-mercury compound, containing a trivalent radicle, and related to iodoform in the same way as iodomethide of mercury is to methyl iodide, or di-mercury methylene iodide to methylene iodide.

The numbers experimentally obtained, and those calculated for $CHHg_3I_3$ and $CH_2Hg_2I_2$, differ so little from one another, as shown below, that the former statement with regard to the nature of the insoluble compound, put with caution, may be regarded as not without foundation.

	Experiments.			
	I.	II.	$CHHg_3I_3$.	$CHHg_2I_2$.
Iodine used up	75·72	76·01	76·66	76·05
Mercury	60·79	60·84	60·36	59·88

The formation of this compound is probably due to the presence of iodoform in the original methylene iodide: for that portion of it which was once used in the preparation of mono-mercury methylene iodide does not give any of the insoluble compound with mercury and mercuric iodide. Moreover, when mercury and iodoform are left together in presence of alcohol and exposed to sunlight, there is formed, among others, a yellowish product, which is insoluble in all the ordinary solvents, hot methylene iodide included—and when treated with iodine (after iodoform has been carefully removed) gives iodoform. We may therefore pretty safely conclude that the insoluble body is a compound of iodoform with mercury, and that we now possess the following series of organo-mercury compounds:—

With methyl iodide..... $CH_3(HgI)$.
„ methylene iodide .. $CH_2(HgI)_2$ and $CH_2(HgI)I$.
„ iodoform..... $CH(HgI)_3$.

Since the first part of this paper was written, some more reactions have been tried with mono-mercury methylene iodide, (CH_2HgI_2), which, though of an unintelligible nature at present, are recorded below.

Strong ammonia, potash, or soda turns this compound grey or almost black, with evolution of heat and separation of metallic mercury. A large quantity of ammonic, potassic, or sodic iodide is formed at the same time. Heated with an aqueous solution of potassic iodide or hydric chloride, it yields mercuric iodomethide; also a brownish insoluble substance, which leaves a black residue on gentle heating.

I wish to record my best thanks to Dr. Williamson for his able assistance, and to Mr. Berry for some of the preparations and analyses.

LXVI.—*Note on the Formation of an Alcoholic Fluoride.*

By Sydney Young, B.Sc., Student in the Laboratory of Owens College, Manchester.

With the exception of a few aromatic compounds, such as benzene and benzoic acid, scarcely a single organic compound has been satisfactorily proved to combine with fluorine. Descriptions of the formation of ethyl and methyl fluoride are indeed to be found in the text-books, but these bodies have never been prepared in a state fit for analysis; and considering the low boiling points which the lower fluorides probably possess, and the necessity of avoiding glass or other materials containing silica, further experiments are perhaps needed before their preparation can be accepted as an accomplished fact. It appeared interesting, therefore, to repeat some of the methods of preparation already tried, as well as others, in order, if possible, to obtain an alcoholic fluoride, and for this purpose the following experiments were made at the suggestion of Professor Roscoe.

Hydrofluoric acid gas was first passed into isobutyl alcohol, and then into the same alcohol to which some zinc fluoride had been added, but no result was obtained by either of these methods.

The next attempt was made by acting on silver fluoride with isobutyl iodide in a closed glass tube, the temperature being allowed to rise to 120° C. the first day, and to 160° the second. On opening the

tube, little or no gas was evolved, but acid fumes smelling like hydrofluoric acid were given off, and the glass was attacked. Before the tube was heated, the brown colour of the iodide, due to a small amount of free iodine, disappeared. The liquid remaining after the experiment had a green colour: it was dried with K_2CO_3 and P_2O_5, and a weighed quantity passed over red-hot lime. The lime was then ignited to get rid of free carbon, when fumes of iodine were evolved. The lime was then dissolved in acetic acid, when scarcely any residue remained, and no trace of fluorine was found. Since free hydrofluoric acid was present, it is possible that some action took place, but that the fluoride could not exist at a high temperature in contact with glass.

A mixture of Nordhausen sulphuric acid, amyl alcohol, and fluorspar was distilled in a glass vessel, this being repeated several times so as to get a pretty large distillate. The latter was, however, of a complicated character, consisting of four layers; the upper one a yellow strong-smelling liquid, then a gelatinous solid, below this a colourless liquid, and at the bottom a colourless solid body. The two liquids also after neutralisation with caustic soda gave complicated distillates.

In order to avoid the presence of silica in the last experiment, a mixture of Nordhausen acid, pure barium fluoride, and amyl alcohol was distilled in a lead vessel. A liquid came over and was collected in a lead vessel, while a certain amount of gas, also given off, was collected over strong sulphuric acid in a glass tube. When the tube was filled, the gas was shaken up with caustic soda to get rid of a little free acid, after which it had a pleasant rather fruity smell. Part of it was absorbed by bromine-water, with formation of oily drops, showing the presence of amylene. The distillate was treated with dilute caustic soda, and the upper liquid separated and dried with potassium carbonate and phosphorus pentoxide. It was then distilled in a glass vessel. At first amylene came over. The temperature then rose gradually to 120°, while fumes were given off, and the glass was attacked, showing the presence of fluorine in the compound. It appears probable that in this reaction amylene is first formed, and that this combines with hydrofluoric acid, forming a fluoride, and it therefore seemed advisable to try the action of gaseous hydrofluoric acid on amylene itself.

The acid was generated in a large lead vessel of the usual form, gypsum being used as a lute. A smaller lead tube was luted to the end of the tube leading from the generator, and this passed into a lead Wolff's bottle fitted with two ordinary corks, and containing a little water to decompose any silicon tetrafluoride that might be formed. The gas was then passed in a similar manner through strong sulphuric acid to dry it, and finally into amylene contained in a large lead

Wolff's bottle surrounded by a freezing mixture. In order to prevent any escape of amylene, a reversed condenser, also of lead, was fitted to the other tubulus of the bottle, a freezing mixture being also employed for this. The end of the tube dipped under strong sulphuric acid, so that any gas that was formed might be collected. The gas proved to be air mixed with a certain quantity of the vapour of amylene, and was not collected after the first two days.

The apparatus was afterwards simplified, as it was difficult to get a good current of hydrofluoric acid to pass through the amylene, and there appeared to be no silica deposited in the first vessel. The gas was therefore afterwards passed only into an empty lead Wolff's bottle to collect any amylene that might run back. The amylene began to fume only after the gas had been passed for several days, or nearly 60 hours. On the last day the corks were attacked, and became very soft. The liquid was neutralised with dry barium oxide and left at rest. A portion was distilled in a glass vessel, when some of the substance came over below 60°, and very little at a higher temperature, the thermometer rising very rapidly to 200°. The thermometer was attacked, and a solid formed in parts of the apparatus. The distillate burned with a blue and rather smoky flame, the mouth of the test-tube being corroded. It also gave off acid fumes.

A portion of the liquid, after its neutrality had been proved, was heated in a test-tube, when the vapours were found to be strongly acid.

A little of the liquid was placed in a glass bulb, and this in a combustion-tube containing pure lime. The vapour was passed over the red-hot lime, and the latter, after burning off the deposited carbon, was dissolved in acetic acid. A residue remained, and was filtered off, washed, and dried. When it was heated with strong sulphuric acid in a platinum basin, fumes of hydrofluoric acid were given off, and a watch-glass was etched.

After this, many attempts were made to estimate the quantity of fluorine in the compound by the above method, the solution of calcium acetate containing free acetic acid being evaporated on the water-bath and heated till no smell of acetic acid remained. This was necessary, on account of the slight solubility of calcium fluoride in acetic acid. No satisfactory results could, however, be obtained by the method, except that the presence of fluorine was always proved by the etching test. The percentage of fluorine given by the method was—as shown by later experiments—always too high, and varied from 6·87 in the original compound, to 18·98 in a distillate obtained under reduced pressure. The calculated percentage of fluorine in amyl fluoride is 21·11. The method cannot be very exact, as the vapour of the substance attacks glass at a high temperature, whereby silicon tetrafluoride is

formed, and this, if decomposed by the lime, would deposit silica, and so give too large a residue.

An attempt was made to obtain a fixed boiling point by heating in a platinum vessel under reduced pressure, the thermometer being placed in a small lead tube, closed at one end, and fitting into the cork which was inserted in the vessel; but the temperature rose without stoppage to above 200°.

The substance was not acted on by sodium-amalgam, or by nascent hydrogen formed by adding a few drops of water to the mixture of liquid and amalgam. On treating some of the substance with bromine, the latter was immediately absorbed, showing the presence of the polymerides of amylene.

About half a pound of amylene was next heated with hydrofluoric acid gas, a rather larger generator being used, and a sulphuric acid lute being employed. In this case, as there was no fear of the amylene running back, the gas was passed directly into the amylene, the latter being, as before, surrounded by a freezing mixture, and a reversed condenser being used. The gas was passed in for about 60 hours, and the strongly fuming liquid neutralised with dry barium oxide. There was always a considerable loss of substance by this process, as the barium fluoride formed a pasty mass, and enclosed a quantity of the liquid. Some of this was, however, recovered by adding water, when part of the liquid collected at the surface, and was poured off. A little barium oxide was again added to remove water.

A combustion of the neutral liquid, made with lead chromate, gave:—

C	80·61
H	13·75
F	5·64 by difference.

There was thus 26·72 per cent. of amyl fluoride, and 73·28 of amylene and its polymerides. The percentage of hydrogen required for this mixture was 13·73.

All the substance was then placed in a lead vessel connected with a Liebig's condenser, the inner tube being of coarse lead, and was distilled from a paraffin-bath. The temperature rose pretty rapidly to 92°, at which point the thermometer remained stationary for some time, while the temperature of the bath rose from 110° to 130°, the liquid during this time being heard to boil. The temperature rose very gradually to 97°, when the apparatus was allowed to cool, and the distillate collected. On again heating, the temperature rose quickly to about 97°, then very slowly to 105°, and afterwards more rapidly to 132°, when the second distillate was collected. The distillates were small compared with the residue, the vapour from which was distinctly acid.

The three portions were treated with barium oxide, and burnt, with the following results:—

(1.) Distillate below 97°—

	(1.)	(2.)	(3.)
C	76·74	76·44	76·72
H	14·39	14·17	14·37
F (by difference)..	8·87	9·39	8·91
	100·00	100·00	100·00

(2.) Distillate between 97° and 132°—

C.....	78·81
H.....	13·84
F.....	7·35
	100·00

(3.) Residue—

	(1.)	(2.)	(3.)
C	83·75	82·74	84·14
H	14·06	14·05	14·00
F	2·19	3·21	1·86
	100·00	100·00	100·00

The above numbers show that when much fluorine was present, the hydrogen came out too high. Thus the percentages of carbon and hydrogen in amylene or its polymerides, and in amyl fluoride, are respectively—

Amylene.		Amyl fluoride.	
C	85·71	C	66·66
H	14·29	H	12·22

The hydrogen should therefore lie between 14·29 and 12·22.

It was found that the glass was much attacked where the vapour of the substance first came in contact with it, and also at the end of the tube next the calcium chloride tube, a deposit of silica being formed. The latter tube was also slightly attacked, especially the first portion, while the water was always distinctly acid. If the acidity were due to hydrofluoric acid, the glass should, however, have been more strongly corroded, and it therefore seemed probable that the acid was hydrofluosilicic acid. That this was really the case was proved by shaking a couple of drops of the water on a watch-glass, and adding barium chloride. No precipitate formed at first, but on evaporating to dryness on a water-bath and adding water, a white crystalline precipitate remained behind, and this was only partially soluble in hydrochloric acid, and was increased in quantity by adding alcohol.

It appears then that the vapour acts on the strongly heated glass, forming silicon tetrafluoride, which is not completely decomposed by the hot lead chromate, but is acted on by the water formed by the oxidation of the hydrogen in the compound, and thus silica is deposited and hydrofluosilicic acid is formed, and some of this distils over with the water into the calcium chloride tube. The potash in the bulbs would, however, not be affected by this, and the carbon may therefore be assumed to be correct. In order therefore to obtain the true composition of the substance analysed, the following correction is made :—

We have the theoretical percentage composition of the fluoride and of amylene respectively :—

Fluoride .. C = 66·66 H = 12·22 F = 21·11 (H + F = 33·33)
Amylene .. C = 85·71 H = 14·29

In the compounds analysed also we have—

$$C = \alpha. \qquad H + F = 100 - \alpha.$$

Thus in the first case, where we have C = 76·74, and H + F = 23·26, if we take x = percentage of amyl fluoride and y = percentage of amylene in the compound, we get the equations :—

$$\begin{aligned}
(1.)\quad & 66{\cdot}66x + 85{\cdot}71y = 7674 \\
(2.)\quad & 33{\cdot}33x + 14{\cdot}29y = 2326 \\
& 33{\cdot}33x + 42{\cdot}85y = 3837 \\
& 28{\cdot}56y = 1511 \\
& \therefore y = 52{\cdot}90 \\
& x = 47{\cdot}10
\end{aligned}$$

From this we get the percentage of fluorine in the compound to be—

$$\frac{21{\cdot}11 \times 47{\cdot}10}{100} = 9{\cdot}94;$$

the percentage of hydrogen in the fluoride to be—

$$\frac{12{\cdot}22 \times 47{\cdot}10}{100} = 5{\cdot}76;$$

and the percentage of hydrogen in the amylene to be—

$$\frac{14{\cdot}29 \times 52{\cdot}90}{100} = 7{\cdot}56.$$

Thus the total hydrogen is 13·32 in the place of 14·39 as found, while the whole adds up to 100; thus :—

C	76·74
H	13·32
F	9·94
	100·00

This correction was used in all the analyses.

The previous analyses thus become—

(1.) Portion coming over below 97° :—

	(1.)	(2.)	(3.)	Mean.
C	76·74	76·44	76·72	76·63
H	13·32	13·19	13·32	13·28
F	9·94	10·37	9·96	10·09
	100·00	100·00	100·00	100·00

Hence the percentage of fluoride was 47·67.

(2.) Portion coming over between 97° and 132° :—

C	78·81
H	13·54
F	7·65
	100·00

showing the presence of 36·22 per cent. of amyl fluoride.

(3.) Residue :—

	(1.)	(2.)	(3.)	Mean.
C	83·75	82·74	84·14	83·54
H	14·08	13·97	14·13	14·06
F	2·17	3·29	1·73	2·40
	100·00	100·00	100·00	100·00

where the percentage of amyl fluoride is only 11·34.

A further distillation was then made in an apparatus consisting of a lead tube 1 inch wide and 6 inches long, burned in at the bottom, and provided with a narrow side-tube 2 feet long, passing through a Liebig's condenser, and bent at the end so as to dip into a small wider lead tube. The large tube was provided with a perforated, tightly-fitting cork, in which was inserted a narrow lead tube, closed at the bottom, and in this was a thermometer. The two distillates—below 97° and between 97° and 132°—were placed together in the vessel, as the quantity was not large enough to work with both separately, and the percentage of fluorine was considerable in both.

The paraffin-bath was then heated to 95°, and the vessel inserted. The temperature rose quickly at first, then more slowly, until the thermometer stood constantly at 72°, while the temperature of the bath rose from 122° to 129°. After this it rose very slowly to 73°, when the distillate was removed. The thermometer now rose very slowly to 81°, when the next portion was removed. Both distillates were light, colourless bodies, having a penetrating ethereal smell, while the residue was, as before, a heavy yellowish oily liquid, having

a smell like that of the polymerides of amylene, with a slight odour of garlic, due to the fluoride.

The vapour this time was not acid, so that it appears to be possible to distil the fluoride, when moderately pure, in lead vessels without decomposition.

The portion boiling at 72° was again distilled, but the quantity was too small to get a constant boiling point in a lead vessel. The portion coming over below 73° was again separated, while the remainder (if any) boiling between 73° and 80°, was collected with that from the previous distillation.

Owing to the large proportion of the polymerides of amylene present, and the consequently small quantity of amyl fluoride, and to the difficulty of working with lead apparatus, it was found necessary in the cases in which a constant boiling point was obtained, to collect any liquid that distilled over before the point was reached, together with that coming over at the constant temperature. Thus any amylene still remaining unacted on became mixed with the liquid boiling constantly at 72°. This will be seen by the following analyses, as well as by the fact that bromine was still absorbed by the liquid.

Composition of liquid coming over at and below 72—73° :—

		(1.)	(2.)
Found—	C	75·23	75·44
	H	15·10	14·54
	F	9·67	10·02
		100·00	100·00

		(1.)	(2.)
Corrected—	C	75·23	75·44
	H	13·15	13·18
	F	11·62	11·38
		100·00	100·00

Mean—	C	75·34
	H	13·16
	F	11·50
		100·00

In this the percentage of amyl fluoride had risen to 54·47.

Composition of liquid coming over between 73° and 80° :—

Found—	C....	72·62	Corrected—	C....	72·62
	H....	13·89		H....	12·87
	F....	13·49		F....	14·51
		100·00			100·00

This portion was the purest obtained, containing no less than 68·73 per cent. of amyl fluoride.

The above experiments show clearly that a fluoride of the fatty group may be formed by the direct union of hydrofluoric acid gas with an olefine. Amyl fluoride thus obtained is a light, limpid, volatile liquid, having an ethereal smell, which, when the polymerides of amylene are present, has some resemblance to that of garlic, but becomes much purer, and more like chloroform when freed from them. Its boiling point lies between 92° and 72°, and is therefore lower than that of the chloride. It appears to be a fairly stable body, no decomposition having taken place on boiling in lead, until the presence of the polymerides raised the boiling point to 130° or thereabouts.

These experiments will be repeated at some future time with larger quantities of amylene, when it is hoped that by more systematic fractional distillation than has yet been possible, the pure fluoride may be obtained, and its properties studied more exactly.

I am much indebted to Mr. Carey, of Messrs. Gaskell, Deacon, and Co., Widnes, for his kindness in supplying me with the lead apparatus, without which it would have been impossible to carry on the above experiments.

LXVII.—*Contributions to the History of the Mineral Waters of Yorkshire. From the Laboratory of the Yorkshire College.*

Communicated by T. E. Thorpe, Ph.D., F.R.S.

Probably no part of England, or indeed of the British Isles, is so rich in remarkable mineral springs as Yorkshire. The virtues of the Harrogate waters have been known and esteemed for more than three centuries, since the discovery, in fact, of the Tewitt Well by Captain Slingsby, in 1570. The Old Sulphur Well is still without a rival among hepatic waters. So far as is known, no water in the world is so strongly chalybeate as the Chloride of Iron Spa of Harrogate; indeed there are only two other springs in Europe which are believed to contain this particular salt of iron: they are the Selken-brunnen at Alexisbad, and the water of Bahowina in Silesia. Very remarkable, too, is the existence of relatively large quantities of barium chloride in many of these springs; the presence of this compound in several of the Harrogate waters was first pointed out by Mr. R. Hayton Davis. Perhaps no locality in England can show such an extraordinary sight

as that of the bog field in Harrogate, where, in a space of some half dozen acres springs of the most widely different character—magnesian, sulphuretted, chalybeate, &c.—are found to rise within a few yards of bases each other.

Among the other notable waters in Yorkshire may be mentioned those of Askern, Thorp-Arch, Croft, Scarborough, and Hovingham. Some of these are not much known beyond the borders of the county, and many of them have not yet been analysed.

It is desirable for various reasons that frequent examinations should be made of many of these waters. Their therapeutic value is undoubted, but it is only within the last quarter of a century that chemical analysis has been sufficiently advanced to enable us to ascertain the nature and amount of their constituents. To what extent their composition is liable to change has still to be made out; we have practically no absolutely trustworthy evidence on this point. So far, however, as it goes, it would seem that the principal Harrogate waters have suffered very little alteration during the present century at least. The Old Sulphur Well, for example, has apparently continued to pour out its saline solution, containing upwards of a thousand grains to the gallon, at an almost uniform rate of flow, and of an almost uniform temperature, since its examination, nearly 100 years ago, by Dr. Joshua Walker.

I hope from time to time, as opportunity serves, to submit to the Society the results of further analyses made in the laboratory of the Yorkshire College, of the mineral waters of the county. It is almost certain that in the future no mineral waters will be more frequently examined than those of this district; we may thus hope, in time, to accumulate information concerning many points in chemical geology, which, as Bischof has shown, can only be elucidated by the careful periodical study of the composition of mineral waters.

I. The Old Sulphur Well, Harrogate.

This water was carefully analysed by me in 1875, and the results were published in the *Philosophical Magazine* of that year (*Phil. Mag.* [5], **2**, 50). It may serve to render the chemical history of the waters of this district more complete if I here reproduce the analytical results; for the details I must refer to the original paper.

Temperature of water (August, 1875)	10°
Specific gravity at 16·8	1011·04

In the quantitative analysis at least two determinations of each principal constituent were made. The results are as follows:—

			Parts per 1,000.
1.	Fixed constituents dried at 170—190°		14·7940
2.	Chlorine		8·6724
3.	Bromine		0·02805
4.	Iodine		0·00146
5.	Carbonic acid (total)		0·5003
6.	Lime and baryta		0·6154
7.	Magnesia (total)		0·3368
8.	Lime and baryta in boiled water		0·3795
9.	Lime precipitated on boiling:—		
	Total lime and baryta	0·6154	
	Lime and baryta retained in solution on boiling	0·3795	
	Lime precipitated on boiling	0·2359	
	Equal to calcium carbonate		0·4206
10.	Lime retained in solution after boiling:—		
	Lime and baryta	0·3795	
	Deduct baryta	0·0683	
	Lime	0·3112	
11.	Baryta		0·0683
12.	Lithium chloride		0·01064
13.	Potassium chloride		0·13553
14.	Sodium chloride		12·7034
15.	Ammonium chloride		0·01457
16.	Silica		0·0099
17.	Total sulphur		0·0923

18. In order to determine the ratio between the dissolved sulphuretted hydrogen and the alkaline sulphide present, I followed the procedure adopted by Simmler in his analysis of the Stachelberg sulphur-water, of expelling the hydrogen sulphide by a current of hydrogen, and passing the escaping gas through an ammoniacal solution of silver nitrate, converting the precipitated sulphide into chloride, and determining the amount of sulphur from the weight of the latter compound.

Dissolved hydrogen sulphide.... 0·0533

19. Determination of alkaline sulphide:—

Total sulphur		0·0923
Equal to H_2S		0·0980
Deduct free H_2S		0·0533
Combined H_2S		0·0447
$= NaHS$	0·07369	

The results of the analysis, arranged according to the conventional mode of representing the state of combination of the various acids and bases are as follows :—

	In 1,000 grams. grams.	In 1 gallon. grains.
Barium chloride	0·09277	6·566
Strontium chloride	traces	traces
Calcium chloride	0·61649	43·635
Calcium fluoride	traces	traces
Calcium phosphate	traces	traces
Magnesium chloride	0·68212	48·281
Potassium chloride	0·13535	9·592
Lithium chloride	0·01064	0·753
Ammonium chloride	0·01457	1·031
Sodium chloride	12·62657	893·670
Sodium sulphydrate	0·07369	5·215
Magnesium bromide	0·03226	2·283
Magnesium iodide	0·00160	0·113
Calcium carbonate	0·42061	29·768
Magnesium carbonate	0·08410	5·953
Silica	0·00991	0·701
Alumina and organic matter	traces	traces
	14·80086	1047·561

The following table shows the results of the various analyses of this spring, made since its examination by Walker, in 1783. The numbers have been reduced to parts per 1,000 :—

Analyst Date	Walker. 1783.	West. 1823.	Hunter. 1830.	Hofmann. 1853.	Muspratt. 1867.	Davis. 1872.	Thorpe. 1875.
Temperature	8·8° C.	—	—	9·0° C.	—	9·4° C.	9·0° C.
Specific gravity	—	1013·24	—	1011·13	—	1011·16	1011·04
Lime	—	0·5614	0·6148	0·6844	0·6533	—	0·5468
Magnesia	—	0·2073	0·2543	0·3313	0·3871	—	0·3370
Baryta	—	—	—	—	0·05201	—	0·0683
Lithia	—	—	—	—	trace	—	0·00376
Potash	—	—	—	0·4785	0·6240	—	0·08569
Ammonia	—	—	—	—	—	—	0·00464
Soda	—	6·2860	6·6560	6·6990	6·6510	—	6·7410
Chlorine	—	8·8000	8·5920	9·1890	9·2550	8·700	8·6740
Bromine	—	—	—	trace	trace	—	0·02805
Iodine	—	—	—	trace	trace	—	0·00145
Sulphur	—	—	—	0·08978	0·09521	0·09061	0·09230
Carbon dioxide	—	—	—	—	—	—	0·05003
Silica	—	—	—	0·00340	—	—	0·00993
Sulphuric acid	—	absent	absent	0·001424	absent	—	absent
Residue on evaporation	15·7000	14·4500	14·3500	15·5000	15·6700	14·7900	14·8000
Free H_2S	—	—	—	0·07504	0·09902	—	0·1435
Free CO_2	—	—	—	0·3113	0·3611	—	0·5666

II. The Chloride of Iron Spa, Harrogate.

By C. H. Bothamley, Assistant Lecturer on Chemistry.

The history of this remarkable spring, which is also known as the Imperial Chalybeate Saline Water, has been carefully investigated by Mr. R. Hayton Davis (*Pharm. Journ.* [2], **7**, 458). In 1791 Dr. Garnett stated that in a chalybeate water, not far from the Crescent Garden, the iron is dissolved by muriatic acid. Hofmann, in 1854 (*Chem. Soc. J.*, **7**, 161), found ferrous carbonate to the extent of only 4·627 grains per gallon, and no ferrous chloride. In 1865 Muspratt (*Chem. News*, **12**, 83) announced the discovery in the water of a considerable quantity of ferrous chloride, and this was confirmed by Dr. W. A. Miller. There would, however, appear to be little doubt that Dr. Garnett was really the discoverer of the existence of this compound in the water. On the other hand we cannot suppose that it would have been overlooked by Hofmann, if present at the time when he made his analysis. In 1872 Mr. Hayton Davis made a series of monthly determinations of the total solids, chlorine, and ferrous chloride and carbonate (this Journal, 1873), but notwithstanding the unique character and high reputation of the spring, no complete analysis has been made since that by Muspratt (*Chem. News*, **13**, 26).

The well is situated about 15 yards west by south from the pump from which the water is served, and is under the road to the northern entrance to the pump-room. This road has been raised several feet above the top of the hill. The well is circular, about 5 feet in diameter, the sides being walled up with dressed stones, and the top covered by two large flagstones. The total distance from the present surface of the road to the bottom of the well is about 28 feet. The water springs from the bottom of the well; its average depth in the latter is about 10 feet, and no variation in the yield can be observed at different seasons. Further, no alterations have been made in the structure of the well for at least 30 years.*

The water for examination was drawn from the pump-room, March 13th, 1880, care being taken to continue pumping sufficiently long to ensure the removal of all water standing in the pipes before collecting that required for analysis. It had a neutral reaction, gave a deep blue coloration with potassium ferricyanide, but no reaction with potassium thiocyanate, thus proving the absence of any ferric salt. When first drawn, the water was perfectly clear and colourless, but on standing bubbles of gas slowly made their way to the surface, and in

* For these details respecting the well I am indebted to Mr. Nicholas Carter, of Harrogate.

a short time the water became turbid, owing to the precipitation of ferric hydrate. The temperature of the water was 7·2° C. (45° F.), that of the air at time of collecting being 10° C. (50° F.); specific gravity at 15° compared with water at the same temperature = 1·005447, a number somewhat lower than that given by Hayton Davis, in 1872, 1·00627; and somewhat higher than that found by Miller, in 1865, 1·00509.

The total solid residue was estimated by evaporating a weighed quantity of the water with pure freshly ignited sodium carbonate in glass flasks of about 4 oz. capacity, with short wide necks, and drying at 170—180°. The flasks were provided with india-rubber corks, so that the residues could be weighed without exposure to air. This plan is much preferable to the usual method of evaporation and weighing in open dishes.

Iron, Manganese, and Silica.—The water for the determination of these constituents was collected in bottles of known capacity, which were filled up to the neck and carefully stoppered. The contents of a bottle (about 1200 c.c.) were evaporated to dryness in a platinum dish with addition of hydrochloric acid, in order to separate the silica, which was filtered off and weighed. The iron was then oxidised by means of bromine-water, and precipitated by ammonia. The precipitate was filtered off, re-dissolved in hydrochloric acid, a few drops of bromine-water added, and the iron again precipitated by ammonia, ignited, and weighed. After correcting for the manganese present, three independent determinations gave:—

	I.	II.	III.	Mean.
Fe per 1,000 grams	0·1582	0·1597	0·1581	0·1587

The manganese, which was precipitated along with the iron, was estimated volumetrically by Chatard's process (*Chem. News*, **24**, 196). The ignited precipitate was finely powdered, and a weighed portion heated strongly in a porcelain boat in a current of hydrogen until no further reduction takes place.

The reduced oxides were then transferred to a small flask and boiled with lead dioxide and nitric acid free from chlorine, diluted with about three times its volume of water. The undissolved matter was allowed to settle and the purple solution was carefully decanted on to a glass-wool filter. This process was repeated until the clear liquid had only a very faint pink tinge. The quantity of permanganic acid found was estimated by means of a dilute solution of ammonium oxalate (100 c.c. = 0·00087 mm.). The liquid should be perfectly clear, since the presence of even a small quantity of suspended matter seriously interferes with the accurate determination of the end-point of the reaction. In consequence of the dilution of the solutions, the reaction

is somewhat slow, and some little time should be allowed to elapse between each addition of the oxalate solution. Two totally independent determinations by this method gave :—

	I.	II.	Mean.
Manganese per 1,000 grams	0·00631	0·00572	0·00602

Ferrous Chloride and Carbonate.—One litre of the water was boiled for half an hour. The almost black precipitate thus obtained contained iron, but no trace of calcium or magnesium ; both these latter elements were therefore present entirely as chlorides. In order to determine whether the method furnished accurate data as to the relative proportions of ferrous chloride and carbonate present in the water, a neutral solution of ferrous chloride was prepared by dissolving 0·4 gram crystallised ferrous sulphate and 0·3 gram, a slight excess, of barium chloride in 500 c.c. of water recently boiled and allowed to cool in an atmosphere of carbonic anhydride. 2·0 grams pure sodium chloride, and 0·7 gram calcium chloride, approximately the quantities present in half a litre of the mineral water, were then added, and the solution was treated with a small quantity of freshly precipitated and well washed barium carbonate, in order to ensure the absence of any ferric salt. After standing for some time, the clear liquid, which had a neutral reaction and gave no coloration with potassium thiocyanate, was syphoned off and boiled in a flask with exposure to air : an abundant dark brown, almost black, precipitate was thrown down. *An artificially prepared solution, having approximately the composition of the water under examination, but containing no ferrous carbonate, became turbid on boiling.*

Several years ago Mr. R. Phillips pointed out (*Pharm. Journ.*, **4**, 207) that when a neutral solution of ferrous chloride is exposed to the air, it is decomposed, with precipitation of ferric oxide, and becomes acid owing to the formation of hydrochloric acid. He regards the presence of air as essential to the decomposition, and states that this decomposition takes place much less readily when the ferrous chloride is dissolved in alcohol, and not at all when it is dissolved in syrup. The following experiments were made with a view to obtain further evidence concerning this decomposition.

0·41 gram crystallised ferrous sulphate and 0·32 gram barium chloride were dissolved in 500 c.c. of water recently boiled and allowed to cool in an atmosphere of coal-gas. A small quantity of barium carbonate was then added and the liquid left at rest. The clear solution, which was perfectly neutral and contained no ferric salt, was syphoned off and boiled in presence of air. A precipitate, at first red, but rapidly changing to very dark brown, was thrown down.

0·5 gram ferrous sulphate and 0·4 gram barium chloride were dissolved in 500 c.c. boiled water, and the solution treated as in the pre-

vious experiment, but the clear liquid obtained was boiled in a current of coal-gas. A precipitate was thrown down which was at first reddish-brown, but eventually changed to almost black. The solution contained no ferric salt either before or after boiling. Before boiling it was perfectly neutral, but after boiling it had a faint but distinct acid reaction. The liquid was filtered and again boiled, when a further slight precipitate was formed. After addition of a few drops of nitric acid, the clear liquid gave a deep blue coloration with potassium ferrocyanide, thus showing that all the iron had not been thrown down. The precipitate formed on boiling dissolved in dilute sulphuric acid without evolution of gas; the solution contained ferrous and ferric sulphates, but was free from chlorine. The precipitate was in all probability hydrated triferric tetroxide.

3·0 grams of clean iron wire were heated in a small flask with a quantity of dilute hydrochloric acid insufficient to dissolve the whole of the iron. The flask was fitted with a cork pierced with three holes, through two of which passed the entrance and exit tubes for a stream of carbonic anhydride, which was led through the flask, whilst the third held a pipette by means of which, when all action had ceased, a dilute solution of pure caustic soda was added drop by drop until a slight permanent precipitate was produced. This precipitate was allowed to settle, and then, by means of a current of carbonic anhydride, about 1 c.c. of the clear liquid was driven over into a flask containing 500 c.c. of boiled water, the upper portion of the flask being filled with carbonic anhydride. The dilute solution of ferrous chloride, which had been carefully kept out of contact with the air, was boiled for half an hour in a stream of carbonic anhydride. A reddish-brown precipitate was thrown down, which, after careful washing, was dissolved in nitric acid free from chlorine. The solution gave a decided turbidity with silver nitrate, and the precipitate was therefore probably a highly basic ferric oxychloride. The ferrous chloride solution, before boiling, had a faint but distinct acid reaction; it contained no ferric salt either before or after boiling. A somewhat stronger solution, obtained in the same way, gave, on boiling, a dark brown precipitate, which dissolved in hot dilute sulphuric acid with formation of ferric sulphate: its solution contained only a trace of ferrous sulphate, and gave only a very faint opalescence with silver nitrate.

These experiments prove that when a dilute neutral or slightly acid solution of ferrous chloride is boiled in presence of air, carbonic anhydride, or coal-gas, it is partially decomposed, with formation of a precipitate, the composition of which depends on the degree of concentration and acidity of the solution. It is evident therefore that merely boiling a mineral water containing ferrous chloride and carbonate, will not give accurate data as to the relative proportions in

which these two compounds are present.* The method adopted for this purpose was as follows:—500 c.c. of the mineral water were mixed with 50 c.c. of a solution of sodium carbonate containing 101·754 grams per litre, and boiled for 45 minutes. The greenish-white precipitate was filtered off and washed thoroughly with hot water. The filtrate was then evaporated to a small bulk in a silver dish, diluted to 250 c.c., and the excess of sodium carbonate determined in 100 c.c. by means of standard acid. The total quantity of sodium carbonate used, less the quantity required to precipitate the barium, calcium, magnesium, and manganese chlorides, gave the amount required to precipitate the ferrous chloride, and from this the quantity of the latter present in the water could be calculated. Two totally independent and concordant determinations gave:—

	Per 1,000 grams.
Iron present as chloride	0·08716
„ „ carbonate.....	0·07975

These determinations were made with water collected February 19th, 1881. The relative proportions of ferrous chloride and carbonate present in the water in 1880, were calculated from the total amount of iron, on the assumption that the ratio between the two compounds was the same at that time as in 1881.

Alkalis.—The alkalis were separated in the usual way, and weighed together as chlorides. Before proceeding to estimate the potassium, the greater part of the sodium was removed by a modification of Hasselt's method (*Zeit. für Anal. Chem.*, 1880, 156), which has been worked out in this laboratory by Mr. J. Wade. It is based upon the fact that sodium chloride, as is well known, is practically insoluble in concentrated hydrochloric acid, whilst potassium chloride dissolves to an appreciable extent. The mixed chlorides were first thoroughly moistened with concentrated hydrochloric acid. 2 c.c. of the acid were then added, the salt crushed and stirred with a glass rod, and after standing five minutes the acid was decanted off into another dish. Ten repetitions of this treatment sufficed to dissolve out all the potassium chloride, whilst the greater part of the sodium chloride remained undissolved. The acid solution was evaporated to dryness, the residue dissolved in water, and the potassium determined in the usual way as platinochloride.

Barium, Calcium, and Magnesium.—A litre of the water was evaporated to about 350 c.c. with addition of hydrochloric acid, a small quantity of dilute sulphuric acid added, and the liquid allowed to

* The approximate agreement between the results obtained by Mr. Hayton Davis (*loc. cit.*) may be explained by the fact that he always took the same volume of water and boiled it for the same time.

stand for several hours. The precipitated barium sulphate was washed well with hot water and weighed. Two determinations gave :—

	I.	II.	Mean.
Barium per 1,000 grams..	0·05183	0·05155	0·05169

The calcium and magnesium were estimated in 500 c.c. of the water in the usual way, after removal of the silica, iron, and barium.

	I.	II.	Mean.
Calcium per 1,000 grams....	0·4815	0·4819	0·4817
Magnesium „ „	0·2078	0·2053	0·2065

The results obtained are given, in grams per 1,000 grams, in the following table. At least two, and in some cases three, determinations of each principal constituent were made:—

Residue on evaporation	6·8167
Chlorine	4·2369
Carbonic anhydride (total).....	0·4274
Bromine	0·00425
Iodine	trace
Silica.....	0·0201
Sulphuric acid (SO_4)	0·0013
Ammonium (NH_4)	0·00195
Barium.....	0·0506
Calcium.....	0·4817
Copper	trace
Iron	0·1587
Lithium.....	trace
Magnesium	0·2066
Manganese	0·00602
Potassium.....	0·0239
Sodium.....	1·5536
Strontium.....	0·00489

In the following table the bases and acid radicles are arranged in the conventional way :—

	Grams per 1,000 grams.	Grains per gallon.
Ammonium chloride	0·00577	0·406
Barium chloride	0·07394	5·204
Barium sulphate	0·00316	0·222
Calcium chloride	1·33580	94·015
Copper chloride	trace	trace
Ferrous carbonate	0·15700	11·050
Ferrous chloride	0·18773	13·213
Lithium chloride	trace	trace
Magnesium bromide	0·00489	0·344
Magnesium chloride	0·81435	57·315
Magnesium iodide	trace	trace
Manganese chloride	0·01379	0·971
Potassium chloride	0·04553	3·205
Sodium chloride	3·94367	277·561
Strontium chloride	0·00886	0·624
Silica	0·02009	1·414
Total residue on evaporation	6·8165	479·754

The volume of free carbonic anhydride was calculated from the total amount, determined in the usual way, after deducting that existing in combination with iron as ferrous carbonate:—

Cubic cent. per 1,000 grams	192·088	At 7·2° C. (45° F.) and 760 mm.
Cubic inches per gallon	53·551	

Careful search was made for cæsium, rubidium, thallium, arsenic, zinc, and phosphoric acid, but these substances could not be detected in the residue from 20 litres of the water. Nitrites and nitrates were also absent.

Water collected March 3rd, 1879.

For this sample of water I am indebted to Mr. Nicholas Carter, of Harrogate. It had been bottled by the method adopted for bottling champagne, and when opened on January 4th, 1881, a year and ten months afterwards, was still perfectly clear, a fact which proves the possibility of bottling this water for transport without fear of its undergoing any alteration. The results of the analysis, as far as the quantity of water at my disposal would permit, were as follows:—

	Per 1,000 grams.
Total residue	7·1280
Chlorine	4·3791
Iron	0·1618
Calcium	0·4804
Magnesium	0·2170

Water collected February 19th, 1881.

During the fortnight immediately preceding the collection of this sample, the rainfall had been somewhat heavy. The results of analysis were as follows:—

Per 1,000 grams.			Per 1,000 grams.	Grains per gallon.
Cl	4·4217	Barium chloride	0·0834	5·873
SiO_2 ..	0·0195	Calcium chloride	1·3564	95·464
Fe	0·1669	Ferrous carbonate	0·1651	11·622
Ba	0·0550	Ferrous chloride	0·1975	13·898
Ca	0·4892	Magnesium chloride	0·8182	57·587
Mg....	0·2069	Manganese chloride	0·0122	0·860
Mn	0·0053	Sodium and potassium chlorides	4·6328	326·060
K and Na	1·8658	Silica	0·0198	1·396
		Total residue	7·2694	511·594

The following table gives, in grams per 1,000, the amount of the principal constituents as determined at different periods since Hofmann's analysis in 1854.

	1854. Hofmann.	July, 1865. Muspratt.	Nov., 1865. Miller.	Jan., 1866. Muspratt.
Total residue	4·0838	6·4461	6·6159	6·6099
Chlorine	2·3987	4·0272	4·1051	4·1048
Iron	0·0319	0·2099	0·1679	0·1723
Calcium	0·3091	0·6432	0·7090	0·6845
Magnesium	0·1228	0·3042	0·3030	0·3042
Barium.....	—	—	0·0635	0·0722
Sodium.....	0·8921	1·1649	1·1507	1·1649
Potassium.....	0·2049	0·0137	0·0286	0·0298

	1872. Davis.	1874. Carnelley.	Mar., 1879. Bothamley.	Mar., 1880. Bothamley.	Feb., 1881. Bothamley.
Total residue	7·6800	—	7·1280	6·8167	7·2694
Chlorine	4·7987	—	4·3791	4·2369	4·4217
Iron	0·2636	0·2903	0·1618	0·1587	0·1669
Calcium	—	—	0·4804	0·4817	0·4892
Magnesium	—	—	0·2170	0·2066	0·2069
Barium.....	—	—	—	0·0506	0·0550
Sodium.....	—	—	—	1·5535	1·8658
Potassium	—	—	—	0·0239	

It is evident, as Hayton Davis has previously pointed out, that this water is liable to considerable and irregular variations in composition.

At the same time the analyses show that only very slight changes have taken place during the last two years. The amount of iron existing in the water at the present time is very nearly the same as that found by Miller in November, 1865, the total solids and chlorine are somewhat higher, and the amount of sodium has increased considerably, whilst calcium and magnesium are present to the extent of only two-thirds the amount in which they existed at that time. The quantity of total solids, chlorine, and iron, seems to have been at a maximum about 1872–74. As in the other Harrogate waters, barium is present in relatively considerable proportion, but not to the same extent as in the Old Sulphur Well. The following table* (p. 511) gives the results, in grains per gallon, of the different analyses of the chloride of iron water up to the present time.

The analytical examination throws very little light on the origin of the ferrous chloride, the presence of which renders the spring so remarkable. The existence of barium chloride in the water, and the occurrence of barium sulphate in considerable quantity in the cracks and fissures of the sandstones in the district, would indicate a double decomposition between barium chloride and ferrous sulphate. If such is really the case, we should expect that at certain times the water would be free from barium and contain ferrous sulphate, but no evidence of the presence of the latter compound has yet been obtained. Frequent examination of the water might throw some light on this point. The presence of a trace of copper agrees with the theory that the iron has been derived from pyrites, but, on the other hand, the absence of arsenic and zinc is opposed to such a supposition. Probably the water as it rises in the well is the resultant, so to speak, of several small springs flowing into the same underground channel or fissure. The variable character of the water, and the fact that no connection can be traced between the variations of different constituents are in accordance with such a supposition. Periodical investigations similar to those undertaken by Mr. Davis in 1872, but of a more detailed character, would probably furnish valuable information, and lead to a more complete knowledge of one of the most remarkable mineral waters in Europe.

III. The Montpellier Strong Sulphur Well, Harrogate.

By A. E. Wilson and H. Ingle.

Although this spring ranks next in importance to the Old Sulphur Well as a sulphuretted water, it seems to have hitherto received but little attention from chemists.

* This table, with the exception of course of the two last columns, is taken from Mr. Hayton Davis previously referred to.

	Hunter, 1819.	Scudamore, 1820.	Murray, about 1821.	Garnett, about 1821.	Hunter, 1829.	Hofmann, 1854.	Muspratt, July, 1865.	Miller, Nov., 1865.	Muspratt, Jan., 1866.	Bothamley, Mar., 1880.	Bothamley, Feb., 1881.
Ammonium chloride .	—	—	—	—	—	trace	—	—	—	0·406	—
Barium chloride	—	—	—	—	—	—	—	6·78	7·717	5·204	5·873
Barium sulphate	—	—	—	—	—	—	—	—	—	0·222	—
Calcium carbonate...	3·75	8·04	—	8·375	—	7·604	—	—	—	—	—
Calcium chloride	37·50	26·40	36·6875	27·50	43·50	51·629	125·587	138·43	133·642	94·015	95·464
Calcium fluoride	—	—	—	—	—	trace	—	—	—	—	—
Calcium sulphate ...	11·25	2·23	—	2·325	—	—	—	—	—	—	—
Copper chloride	—	—	—	—	—	—	—	—	—	trace	—
Ferrous carbonate...	9·062	4·176	4·35	4·35	7·685	4·627	10·482	11·62	10·482	11·050	11·622
Ferrous chloride	—	—	—	—	—	—	22·014	14·49	16·011	13·213	13·898
Lithium chloride	—	—	—	—	—	—	trace	bare trace	trace	trace	—
Magnesium carbonate	—	0·96	—	1·00	—	—	—	—	—	—	—
Magnesium chloride .	16·25	11·88	13·50	12·375	9·65	34·027	84·716	84·39	84·716	57·315	57·587
Magnesium bromide .	—	—	—	—	—	trace	trace	—	—	0·344	—
Magnesium iodide ..	—	—	—	—	—	trace	trace	—	—	trace	—
Manganese carbonate	—	—	—	—	—	trace	trace	trace	trace	—	—
Manganese chloride..	—	—	—	—	—	—	—	—	—	0·971	0·860
Potassium chloride ..	—	—	—	—	—	27·410	1·842	3·84	4·013	3·295	} 326·060
Sodium chloride	542·50	360·48	364·375	375·50	576·50	158·840	208·468	205·92	208·468	277·561	
Sodium carbonate ..	—	—	10·0875	—	—	—	—	—	—	—	—
Sodium sulphate	—	—	2·425	—	—	—	—	—	—	—	—
Strontium chloride ..	—	—	—	—	—	—	—	—	—	0·624	—
Silica	—	} 0·48	0·5	0·5	—	1·450	0·416	trace	trace	1·414	1·396
Organic matter	loss 3·125				—	0·282	—	—	—	—	—
Residue on evaporation.	623·437	413·315	431·925	431·925	637·335	285·869	453·525	465·47	465·049	479·754	511·594
Specific gravity	—	—	—	—	—	—	—	1·00509	—	1·005447	—

So far as we have been able to ascertain, only three analyses have been made, viz., one by West in 1845, one by Hofmann in 1854, and the third by Attfield in 1879.

The most noticeable point of difference in these analyses is in the state in which the sulphur is supposed to exist in the water. West reports it as uncombined sulphuretted hydrogen dissolved in the water, whilst Hofmann and Attfield both assume it to be contained as sodium sulphide.

The water for the analysis which forms the subject of the present communication, was collected from the pump room on April 2nd, 1880, all due precautions being taken to obtain a representative sample. It was perfectly clear and colourless, and smelt strongly of sulphuretted hydrogen. It had a sparkling appearance, bubbles of carbon dioxide escaping on standing. On free exposure to the air the smell disappeared, and the water became turbid, owing to the separation of sulphur. The temperature of the water as it issued from the pump was 7·5° C., that of the air at the same time being 10·5°. The specific gravity was 1·011152 at 15·5°, compared with distilled water at the same temperature.

The sulphur was determined immediately on drawing the water from the spring, a measured quantity of the water being titrated with a centinormal solution of iodine in the usual way.

In order to determine whether the sulphur existed as free sulphuretted hydrogen or in combination as sulphides, a current of pure hydrogen was passed through a quantity of the water for a considerable time, and the residual sulphur determined by means of iodine and starch-paste. Only a mere trace was found after the hydrogen had been passed through for some hours. Hence it seems that the sulphur does actually exist in the water as uncombined sulphuretted hydrogen, as West reported in 1845.

The amount of barium was ascertained as follows: 19,695 c.c. of the water (the quantity employed in the determination of the constituents present only in small proportions) were evaporated to dryness with hydrochloric acid and a small quantity of sulphuric acid; the residue was moistened with hydrochloric acid and hot water added; and the insoluble portion consisting of barium sulphate and silica was well washed with dilute hydrochloric acid, in order to remove any coprecipitated calcium sulphate, and finally with hot water. It was then dried and fused with a mixture of potassium and sodium carbonates, allowed to cool, treated with large quantities of hot water containing a little ammonium carbonate, in order to dissolve out the sodium and potassium silicates (and sulphates) formed, and the insoluble matter consisting of barium carbonate was filtered off and washed well with water containing ammonium carbonate. The barium carbonate was

then dissolved in hydrochloric acid, precipitated as sulphate by means of sulphuric acid, filtered off, washed, dried, and weighed.

The purity of the barium sulphate was confirmed by again fusing it with the mixture of the alkaline carbonates, treating the fused mass with hot water containing ammonium carbonate, washing the insoluble barium carbonate, dissolving it in hydrochloric acid, and again precipitating with sulphuric acid, when an amount of barium sulphate was formed which, after careful washing with hot water, was identical with that previously obtained.

The amount of barium thus found was 0·08774 gram Ba per 1,000 grams of water, equal to 9·4664 grains $BaCl_2$ per gallon. This is a remarkably large amount, being greater than that found in the Chloride of Iron Spa by Muspratt in 1867 (7·717 grains $BaCl_2$ per gallon), or that in the Old Sulphur Well by Dr. Thorpe in 1876 (6·56 grains $BaCl_2$ per gallon).

The alkalis were determined in the usual way, and the potassium and sodium, after being weighed together as chlorides, were separated by the modification of Hasselt's method described above.

Phosphoric acid, manganese, and sulphuric acid were also sought for, but could not be detected.

A trace of lithium was found in the residue from about 20 litres of the water, but the amount was not determined.

In the following table the amounts of the various constituents are given in parts per 1,000, being the mean of several determinations.

Barium	0·08774
Bromine	0·01114
Calcium	0·50536
Chlorine	8·65580
Iodine	0·0000053
Iron	0·00208
Lithium	trace
Magnesium	0·21016
Potassium	0·04145
Silica	0·03058
Sodium	4·81577
Strontium	0·00174
Total solids on evaporation	14·40095

Volume of sulphuretted hydrogen present in 1,000 grams of water at 7·5° and 760 mm. = 76·097 c.c.

In the following table the results are arranged in the ordinary way :—

	Grams per 1,000.	Grains per gallon.
Barium chloride	0·1337	9·466
Calcium carbonate ..	0·3982	28·193
Calcium chloride	0·7795	55·170
Ferrous carbonate ..	0·0043	0·304
Magnesium bromide .	0·0128	0·905
Magnesium chloride..	0·8316	58·861
Magnesium iodide ..	0·000056	0·00039
Potassium chloride ..	0·0790	5·595
Sodium chloride	12·2275	865·469
Strontium chloride ..	0·0032	0·224
Silica.....	0·0306	2·165
Total	14·5004	1026·352
Volume of SH_2 at 7·5° and 760 mm.	76·097 c.c.	21·335 cub. inches.

In the following table will be found in parts per 1,000, the results of the various analyses of the Montpellier strong sulphur water made since 1845. The amounts of the various constituents were calculated from the tables given by the analysts, in which, with the exception of Hofmann's, the results were stated in grains per gallon of the compounds present.

Hofmann, in addition to such a list, published another in which the amounts per 1,000 of the various acids and bases were given. It was from this latter list that the results given as Hofmann's in the accompanying table were calculated.

Analyst.....	West.	Hofmann.	Attfield.	Wilson and Ingle.
Date	1845.	1854.	1879.	1880.
Ammonium (NH_4)	—	trace	0·00474	—
Barium.....	—	—	0·00276	0·08774
Bromine	—	marked trace	trace	0·01114
Calcium.....	0·4372	0·4547	0·45657	0·50536
Chlorine	8·8730	8·0637	8·49064	8·65580
Iodine	—	marked trace	trace	0·0000053
Iron	—	trace	0·00283	0·00208
Magnesium	0·1843	0·1964	0·20705	0·21015
Nitric acid (NO_3)	—	—	0·00928	—
Potassium.....	—	0·0428	0·03559	0·04145
Sodium	4·9792	4·5865	4·72167	4·81577
Silica.....	—	0·0261	0·05045	0·03058
Strontium.....	—	—	0·02554	0·00174
Sulphur (as H_2S)	0·0952	0·11608	0·08405	0·10618
Sulphuric acid (SO_4)	—	0·0059	0·00635	—
Total residue	—	13·5881	—	14·40095
Specific gravity	—	1·01045	—	1·011152

In the results of West's analysis, the amount of sulphur per 1,000 grams of water was calculated from the volume of sulphuretted hydrogen, which he reported in cubic inches per gallon, assuming it to have been measured at 15·5° C. and 760 mm. pressure.

Hofmann, in his paper on the Harrogate water (*Chem. Soc. J.*, **7**, 161), reports the whole of the sulphuretted hydrogen as sodium sulphide, but also gives the total volume of sulphuretted hydrogen in cubic inches per gallon. Moreover, he gives the weight of the sulphuretted hydrogen present in 1,000 parts by weight of the water, viz., 0·0899, equal to 0·0846 of sulphur per 1,000 parts of water. The volume of sulphuretted hydrogen per gallon, viz., 23·35 cubic inches if we assume it to have been measured at 8° C., the temperature of the spring according to Hofmann, is equal to 0·11608 gram per 1,000 grams of water. This latter result is the one given in the table.

On comparing the analyses contained in the above table, it will be seen that the Montpellier strong sulphur water has not experienced any very marked change in composition since 1845.

The amounts of calcium and magnesium seem to be steadily increasing, the following being the results in grams per 1,000 found by the various analysts:—

Analyst.	West.	Hofmann.	Attfield.	Wilson and Ingle.
Calcium	0·4372	0·4547	0·45657	0·50536
Magnesium ..	0·1843	0·1964	0·20705	0·21015

IV. Boston Spa, Thorp-Arch.

By Caroline L. Kennedy and Margaret N. Johnstone.

The water of this spring issues from the base of a limestone rock on the south side of the river Wharfe, about 300 yards below Thorp-Arch bridge. It was discovered in 1744, and has been frequently noticed by writers on mineral waters.*

The water is bright and sparkling, and slightly effervescent: on standing it becomes turbid. Contrary to Dr. Munro's statement that it has a strong sulphurous smell, it is absolutely free from any sulphurous ingredient. Its reaction is distinctly alkaline. Its temperature at the time of collection, October, 1879, was 9°. Dr. Hunter, in 1819, found 9·4 (49°). Dr. Walker, in 1783, observed 8·6 (47½); its specific gravity at 15°, compared with water at the same temperature, was 1·0071.

The results of its analysis are as follows: the numbers give the amount in grams of the substances obtained from 1,000 grams of the water.

* See Short on "Mineral Waters," p. 56; Donald Monro's "Treatise on Mineral Waters," vi, p. 454; Walker's "Essays;" Hunter's "Observations on the Mineral Spring at Thorp-Arch."

	Grams.
1. Joint amount of silver chloride and bromide..	22·0294
2. Silver chloride	22·0014
3. Silver bromide	0·0280
4. Chlorine	5·4409
5. Bromine	0·0119
6. Carbonic acid (total)	0·3465
7. Sulphuric acid	absent
8. Silica	0·0193
9. Ferric oxide.....	0·0059
10. Barium sulphate.....	0·0189
Barium	0·0111
11. Total lime (CaO)	0·4578
expressed as carbonate	0·8175
12. Magnesium pyrophosphate	0·6040
Magnesia	0·2176
13. Lime in boiled water.....	0·3960
expressed as carbonate	0·7071
14. Mixed alkaline chlorides	7·5654
15. Potassium chloride.....	0·0488
16. Sodium chloride.....	7·5166
17. Total fixed constituents (dried at 150°)	8·8112

These ingredients may be arranged in the following manner:—

	Parts per 1,000.
Barium chloride	0·0169
Magnesium chloride	0·4748
Calcium chloride	0·7848
Magnesium bromide	0·0137
Calcium carbonate.....	0·1104
Magnesium carbonate ..	0·0374
Ferrous carbonate	0·0086
Silica	0·0193
Potassium chloride	0·0488
Sodium chloride	7·5166
	9·0313

The water, in its normal condition, that is, when unmixed with flood water, seems to have changed but little since Dr. Hunter's examination in 1819. At that time a wine gallon evaporated to dryness at a steam heat afforded 584 grains of saline matter, and the sum of the ingredients at the present time is about 527 grains, the difference being probably due to the fact that the temperature employed by Dr. Hunter was not sufficient to expel all the combined water. Neither Dr. Walker nor Dr. Hunter found any evidence of sulphuric acid.

LXVIII.—*Fractional Distillation with a Still-head of Uniform Temperature.*

By Frederick D. Brown, B.Sc., Demonstrator of Chemistry in the University Museum, Oxford.

In a paper on "The Comparative Value of Different Methods of Fractional Distillation" (this Journal, 1880, Trans., 49), I described an apparatus, by means of which the vapour evolved by a mixture of liquids in ebullition could be made to ascend a long tube, maintained at a constant temperature, before passing into the condenser of the distilling apparatus. If the temperature of this tube be less than that of the vapour which enters it from the still, partial or total condensation must take place, resulting in the former case in the return to the still of a mixture richer in the liquid of higher boiling point than the vapour, and consequently in the production of a distillate richer in the liquid of lower boiling point than the same vapour. The process of fractional distillation is therefore improved by the introduction of a still-head of constant temperature, as was shown long ago by Warren (*Memoirs of the Amer. Acad.*, New Series, **9**), a picture of whose apparatus is given in the fifth edition of *Miller's Chemistry*, **3**, Section I, p. 8. Warren's apparatus, though well adapted to all ordinary requirements, is ill-suited to exact scientific experiments, on account of the difficulty of maintaining a constant temperature in the still-head. This difficulty is chiefly due to the continual but irregular heating of the liquid surrounding the still-head by the vapour from the still, this source of heat being often so considerable as to necessitate the use of a current of water to keep down the temperature.

In the apparatus referred to above, and shown on the left hand of the figure accompanying this paper, the heat brought to the still-head by the vapour from the still merely increases the rate of ebullition of the liquid surrounding the coiled tube, and does not raise the temperature, the reading of the thermometer in the still-head being in fact entirely independent of the distillation. Hence it is possible to conduct a long distillation without fear of any variation in the temperature of the still-head, and if necessary, to repeat it, or to make a second with a different mixture at the same temperature.

Although it is generally recognised that the use of Warren's apparatus is very advantageous, the laws which govern the process have hitherto been unknown; it seemed to me therefore to be desirable to submit the whole matter to investigation, more especially as the work promised to yield results of considerable theoretical import-

ance. Thus, in the paper above referred to, four distillations of mixtures of benzene and carbon disulphide were given, in which the temperatures of the still-head were 57·1°, 70·1°, 46·5°, and 46·5° respectively. These distillations resulted in each case in a distillate of uniform composition, while in the last two the distillate consisted of almost pure carbon disulphide, a result which seemed incompatible with the fact that at 46·5° the tension of the vapour of benzene is nearly 240 mm. Postponing till the close of this communication any attempt to explain this and similar anomalies, I proceed at once to describe the experiments which I have made upon the subject.

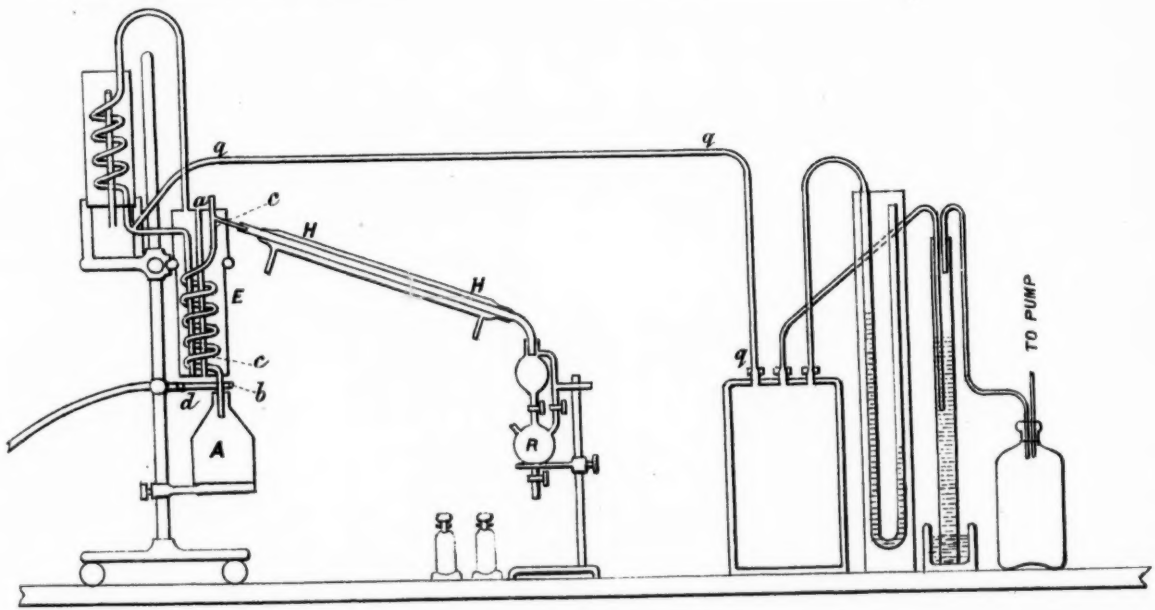
The complete apparatus employed is shown in the figure. A is the still, *cc* the copper coil serving as still-head; E the cylinder surrounding it, and containing some liquid kept in ebullition by the burner *b*; HH the condenser, R the receiver, while the portion to the right of R represents the apparatus for maintaining any constant pressure in the cylinder E, and consequently any constant temperature; this last-mentioned apparatus I have recently described in a paper on "The Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride" (this Journal, 1881, Trans., 304); it communicates with the cylinder E by means of the tube *qqq*. A thermometer, T_1, was placed in the tube *aa*, and a second thermometer, T_2, in the upper end of the coil *cc*. For a more complete description the reader is referred to the papers mentioned above.

The thermometer T_2 was always one which had been compared with the standards used in all these researches, and a correction was made for any difference of reading observed; the index error of the thermometer was also allowed for. The thermometer T_1 being merely employed to show the general absence of variation in the temperature of E, its readings were not corrected. In any case these corrections are not of much value, as the distillations were carried out under the ordinary barometric pressure, and from the nature of the case no reduction could be made to the standard pressure of 760 mm. The general nature of the result is, as will be seen, unaffected by any small errors arising from this cause.

The first experiments were made with mixtures of carbon disulphide and carbon tetrachloride, the composition of which was determined by observing the density, as in previous cases. The liquids were purified with great care, as described before (*loc. cit.*, p. 306).

The burner *b* having been lighted, and the apparatus for constant pressure suitably adjusted, the ebullition of the liquid in E (in this case methylated spirit) was allowed to proceed for a short time until the reading of the thermometer T_1 remained constant. The still A, consisting of a glass flask, and containing about a pint of a mixture of the two liquids, was then adapted to the lower end of *cc*, and gradu-

FRACTIONAL DISTILLATION STILL-HEAD AT UNIFORM TEMPERATURE.



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ally heated, when the mixture began to boil. It sometimes happened that the temperature of its vapour was below that of the still-head; in this case it is evident that the vapour ascended the coil unchanged, and passed into the condenser just as if no still-head were present; but as the mixture in the still became richer in CCl_4, the temperature of the vapour evolved necessarily rose, until it exceeded that of the still-head; partial condensation then took place, indicated by a continual dropping from the lower end of C. Only when this return of liquid to the still became well marked were the fractions tabulated below collected.

As the experiment proceeds, the proportion of CCl_4 in the still increases, the condensation in the still-head becomes relatively greater, and the distillation slower and slower, until at length the whole of the vapour generated in the still condenses in the still-head, and the distillation ceases. The process is therefore limited at both ends, commencing when the boiling point of the mixture in the still equals the temperature of the still-head, and ending when the mixture in the still has reached a certain composition, of which more anon. The fractions, of which the densities and percentage composition (reckoned as in previous papers in molecules) are given in the following table, generally constituted together nearly the whole of the possible distillate, and amounted to a considerable fraction of the whole mixture employed. In each case therefore the mixture in the still varied very greatly in composition during the experiment. In some of the distillations the percentage was determined at the commencement and at the end of the process; where this was done, the results are given in the first column. The thermometers were read at equal intervals of time throughout the experiment, the mean reading for each fraction being given. In other respects the following table of ten distillations requires no explanation:—

General remarks.	Number of fraction.	Reading of therm. T_1.	Reading of therm. T_2 (corrected).	Density of fraction corrected to 20°.	Percentage of CCl_4 in fraction.
A.....	I....	48·65	48·45	1·29894	6·89
	II....	48·65	48·45	1·29803	6·69
	III....	48·65	48·40	1·29732	6·54
	Mean ..	48·65	48·43	1·29810	6·71
B.....	I....	52·00	51·80	1·33820	15·68
	II....	52·00	51·90	1·33835	15·72
	III....	52·00	51·80	1·33788	15·60
	Mean ..	52·00	51·82	1·33814	15·67
C.....	I....	59·37	59·29	1·41425	35·20
	II....	59·37	59·25	1·41379	35·08
	Mean ..	59·37	59·27	1·41402	35·14
D.....	I....	63·65	63·58	1·45925	48·55
	II....	63·69	63·59	1·45893	48·45
	Mean ..	63·67	63·59	1·45909	48·50
E.....	I....	66·34	66·35	1·48740	57·64
F.....	I....	71·87	71·73	1·54502	78·39
	II....	71·84	71·80	1·54487	78·33
	III....	71·82	71·73	1·54607	78·79
	Mean ..	71·84	71·75	1·54532	78·50
H carried to limit....	I....	69·10	68·91	1·51783	68·24
K carried to limit....	I....	69·14	69·00	1·52156	69·59
L carried to limit	I....	56·00	55·80	1·38092	26·32
	II....	56·01	55·82	1·38134	26·21
	Mean ..	56·00	55·81	1·38113	26·27
M carried to limit....	I....	56·18	55·96	1·38653	27·68
	II....	56·13	55·80	1·38549	27·41
	Mean ..	56·15	55·88	1·38601	27·54

An inspection of the above table leads to the conviction that the composition of the vapour issuing from the top of the coil is dependent on the temperature of the coil, and upon that only, remaining constant while the composition of the boiling liquid changes. This result is identical with that foreshadowed by the experiments detailed at the close of my paper referred to above (this Journal, 1880, 58).

We have now to inquire what relation exists between the temperature of the coil and the composition of the distillate.

Referring to the curves expressing the distillation of CS_2 and CCl_4, or to Tables XXVIII and XXIX (this Journal, 1881, 310), we can easily obtain the temperature at which a vapour of particular com-

position is evolved by a mixture of the two substances boiling under the ordinary pressure, or in other words, find the boiling point of that mixture which evolves a vapour of given composition.

In the following table the first column gives the mean composition of the vapour issuing from the still-head in each of the above distillations; the second column gives the temperature of the still-head; the third column the composition of the mixture, which on ebullition evolves vapour, having the composition mentioned in the first; while the fourth column contains the boiling point of such mixture.

Percentage of CCl_4 in vapour as observed.	Temperature of still-head.	Percentage of CCl_4 in mixture evolving vapour given in column I.	Boiling point of mixture mentioned in column III.
6·7	48·4	14·1	48·1
15·7	51·8	32·9	51·5
35·1	59·3	61·3	59·4
48·5	63·6	73·2	63·7
57·6	66·4	80·0	66·5
78·5	71·8	91·6	72·1
68·2	68·9	86·7	69·6
69·6	69·0	87·4	70·0
26·3	55·8	50·7	56·0
27·6	55·9	52·2	56·5

On comparing the numbers in the second and fourth columns, and remembering that no correction has been made for varying barometric pressure, it will be recognised that in the first six cases they are practically identical; in the remaining four cases the agreement is not so good, but this arises from the conditions under which these experiments were made, viz., with a large percentage of CCl_4 in the still and an extremely slow distillation. Under such circumstances it would be expected that the percentage of CCl_4 in the distillate would be somewhat greater than under more usual conditions, and consequently the boiling point of the corresponding mixture higher. We are therefore led to the following general statement:—*In distillations with a still-head maintained at a constant temperature, the composition of the distillate is constant, and is identical with that of the vapour evolved by a mixture whose boiling point equals the temperature of the still-head.* We shall see that this statement is fully confirmed by other experiments made with other liquids.

Before passing to those confirmatory experiments, I should like to draw attention to one or two matters of great practical, though of little theoretical, importance. It has been already mentioned that as the mixture in the still becomes richer in CCl_4, the proportion of the

evolved vapour which is returned to the still rapidly increases, while the remainder which finds its way to the receiver as rapidly diminishes; there is therefore a limit to the proportion of CCl_4 in the still, beyond which distillation becomes impossible.

With a view to ascertain whether this limit was susceptible of any general definition applicable, like the statement given above, to all mixtures of a normal character, the last four distillations, H, K, L, and M, were continued until the delivery of liquid from the end of the condenser dwindled to an occasional drop. The percentage of CCl_4 in the residue in the still was then determined, and was found to be as follows:—

H	99·2
K	99·4
L	93·2
M	91·9

Bearing in mind the fact that with mixtures of carbon disulphide and benzene a mixture containing 38 per cent. of CS_2 was obtained as distillate, when the mixture in the still contained only 4·3 per cent. of CS_2, or 95·7 per cent. of benzene, we are led to the conclusion that the absolute or theoretical limit is reached only when the still no longer contains any of the liquid of lower boiling point, but that this limit becomes more and more difficult to attain, as the temperature of the still-head is reduced. A further prosecution of the enquiry in this direction seemed therefore of little value, more especially as the experiments coincided with the conclusions derived from the explanation of the whole matter, which will be given further on.

A second point of interest was the composition of the mixture returned to the still by condensation in the still-head. With a view to determine this, two distillations were made with a test-tube, suspended below the lower end of the tube *cc*, so as to catch the liquid dropping back; the distillation was interrupted, and the test-tube removed when it was full. During the first distillation the still-head was maintained at 56·8°, and two successive samples of the returning liquid were collected; the first contained 60·4 per cent. of CCl_4, and the second 69·2 per cent. During the second distillation the still-head was kept at 57·1°, and four fractions of the returning liquid were collected; they contained respectively 60·9, 64·8, 68·9, and 74·1 per cent. of CCl_4. Remarking that the first drop which is returned to the still when the vapour which enters the still-head has a temperature equal to or slightly exceeding that of the coil, must have the same composition as the boiling mixture, and that at the limit the returning liquid must be pure CCl_4, we see that the percentage of CCl_4 gradually

increases throughout the distillation, but that it cannot be defined more exactly.

I now pass to a series of experiments with mixtures of carbon disulphide and benzene, which were conducted in a manner precisely similar to those given in the first table in this communication. In the following table the experiments given at the close of the paper on the comparative value of different methods of fractional distillation (*loc. cit.*) are included. The percentages given being those of CS_2, the most volatile liquid, instead of the least volatile, as in the previous case, the table has a slightly different aspect:—

General remarks.	Number of fraction.	Reading of therm. T_1 in cylinder.	Reading of therm. T_2 (corrected).	Density of fractions at 19·80.	Percentage of CS_2 in fraction.
A.....	I....	70·29	69·94	0·98826	38·44
	II....	70·35	69·98	0·98516	37·48
	III....	70·57	70·23	0·98498	37·42
	IV....	70·56	70·24	0·98527	37·52
	Mean ..	70·44	70·10	0·98592	37·71
B. Residue contained 2·4 p. c. of CS_2.	I....	63·81	63·76	1·05305	56·66
	II....	63·73	63·47	1·05606	57·43
	Mean ..	63·77	63·61	1·05456	57·04
C.....	I....	57·50	57·10	1·13523	75·73
	II....	57·50	57·10	1·13185	75·02
	III....	57·50	57·10	1·13348	75·36
	IV....	57·50	57·10	1·13528	75·74
	V....	57·52	57·12	1·13649	75·99
	VI....	57·51	57·10	1·13656	76·01
	VII....	57·53	57·12	1·13733	76·17
	VIII....	57·53	57·30	1·13819	76·35
	IX....	57·53	58·00	1·13358	75·38
	X....	57·53	57·90	1·13333	75·33
	Mean ..	57·52	57·29	1·13513	75·71
D.....	I....	52·74	52·55	1·18001	84·80
	II....	52·74	52·55	1·18008	84·81
	III....	52·74	52·50	1·18058	84·90
	IV....	52·74	52·40	1·18132	85·05
	Mean ..	52·74	52·50	1·18050	84·89
E. Residue contained 17·8 p. c. of CS_2.	I....	49·00	48·92	1·22743	93·43
	II....	49·00	48·83	1·22529	93·05
	III....	49·00	48·85	1·22789	93·51
	Mean ..	49·00	48·87	1·22687	93·33

The above five distillations confirm the statement previously made, that the composition of the vapour issuing from the coil is dependent only upon the temperature of the coil.

The following table corresponds exactly with that given for CS_2 and CCl_4, on page 520, the numbers in the third and fourth columns being obtained from the curves referred to in a paper on "The Theory of Fractional Distillation" (this Journal, 1879, Trans., 547).

Percentage of CS_2 in issuing vapour as observed.	Temperature of issuing vapour.	Percentage of CS_2 in mixture evolving vapour given in first column.	Boiling point of mixture given in third column.
37·7	70·1°	13·3	70·2°
57·0	63·6	26·3	63·6
75·7	57·3	46·9	56·7
84·9	52·5	64·0	52·1
93·3	48·9	83·7	48·6

Comparing the numbers given in the second and fourth columns, we see that they agree fairly well together, thus confirming the general statement made on page 521.

The experiments which yielded the data necessary for determining the above-mentioned curves were made with imperfect apparatus; had the apparatus been of the improved form used in the experiments on mixtures of CS_2 and CCl_4, it is probable that the numbers in the two columns would have been still more nearly equal.

A series of distillations were now made with mixtures of alcohol and water, with a view of ascertaining whether the laws governing the above experiments were also applicable in this case, in which the two substances mixed exert a certain action one upon the other. The cylinder surrounding the coil was filled with water, the boiling point of which was regulated by reducing the pressure as before. The composition of the various fractions, &c., was determined by observing their densities at 20°. The numbers in the following tables give the percentage of alcohol *by weight* and *not in molecules*, as in the previous cases. The densities at 20° of mixtures of alcohol and water have been determined by many persons, and among them by Mendelejeff (*Pogg. Ann.*, **138**, 103 and 230; *Watts's Dict.*, 2nd Supp., 476), whose numbers I have employed to obtain the percentages corresponding to the densities observed.

The table of densities given by Mendelejeff is based on experiments in which the weighings were reduced to a vacuum; it becomes therefore a question of some importance whether this correction must be made in the experiments given below:—

If W_1 = apparent weight of tube + mixture,
„ W_2 = „ „ „ + water,
„ W_3 = „ „ „ empty,

we have D_1 = apparent density = $\frac{W_1-W_3}{W_2-W_3}$. If D = the true density, e = weight of 1 c.c. of air = ·0012 gram, N = the density of the weights, V = volume of air displaced by the empty tube, we have evidently—

$$D = \frac{W_1 + e\left(\frac{W_1-W_3}{D} + M - \frac{W_1}{N}\right) - W_3 - e\left(M - \frac{W_3}{N}\right)}{W_2 + e\left(\frac{W_2-W_3}{1} + M - \frac{W_2}{N}\right) - W_3 - e\left(M - \frac{W_3}{N}\right)},$$

$$\text{or } D = \frac{W_1 - W_3 + e\frac{W_1-W_3}{D} - e\frac{W_1-W_3}{N}}{W_2 - W_3 + e(W_2-W_3) - e\frac{W_2-W_3}{N}},$$

$$\text{or } D = \frac{W_1-W_3}{W_2-W_3}\left\{\frac{1 + \frac{e}{D} - \frac{e}{N}}{1 + e - \frac{e}{N}}\right\}$$

$$\text{or } D = D_1\,\frac{1 + \frac{e}{D} - \frac{e}{N}}{1 + e - \frac{e}{N}}.$$

If in this expression we make N = 8, and D = D_1, we obtain the following corrections to the densities, as observed by weighing in air:—

Densities.	Corrections.
0·79	+ 0·00025
0·85	+ 0·00018
0·90	+ 0·00012
0·95	+ 0·00006
1·00	+ 0·00000

In the following tables corrections are made corresponding with the above, though the error incurred by neglecting them would have been scarcely appreciable.

The densities are referred to water at 4°, and not at 20°. In other respects the distillations correspond exactly to those made with mixtures of CS_2 with CCl_4 and C_6H_6 respectively.

	No. of fraction.	Reading of T_1 in cylinder.	Reading of T_2 in top of coil (corrected).	Density reduced to 20° and corrected for weighing in air.	Percentage of alcohol in fraction.
A.....	I....	77·67	78·40	0·82052	89·05
	II....	"	"	0·82026	89·15
	III....	"	"	0·82006	89·22
	IV....	"	"	0·81963	89·38
	V....	"	"	0·81926	89·56
	Mean ..	"	"	0·81995	89·27
B.....	I....	81·97	81·64	0·85142	76·80
	II....	82·02	81·78	0·85218	76·49
	III....	82·23	81·99	0·85318	76·08
	Mean ..	82·07	81·80	0·85226	76·46
C.....	I....	86·77	86·53	0·87762	65·84
	II....	86·82	86·54	0·87752	65·88
	Mean ..	86·80	86·54	0·87757	65·86

The numbers in the last column of this table show that in this case also the composition of the distillate does not vary when the temperature of the coil remains constant; it will be noticed that in the first experiment A, the proportion of alcohol slightly increased as the distillation progressed; this is due to the more effectual action of the coil upon the ascending vapour as the rate of distillation diminishes. In the second experiment, B, the temperature rose slightly, and consequently the percentage of alcohol diminished from fraction to fraction; the general constancy of the distillate is, however, evident.

It remains for us to learn whether the vapour containing 76·46 per cent. of alcohol issuing from the coil when the temperature is 81·80°, is identical in composition with that which is emitted by a mixture boiling at 81·80°, and the same in the case of the third experiment.

The composition of the vapours given off by spirit of different strengths, together with the boiling points of such mixtures, have been determined by Gröning and many other observers; the discrepancies of the different tables to be found in works on alcoholometry are, however, so great that I thought it simpler to make the necessary experiments myself. With this object the copper still furnished with a jacket, and described by me in a previous paper (this Journal, 1881, Trans., 311), was filled with a mixture of alcohol and water boiling a little below the requisite temperature, and the distillation allowed to proceed until the thermometer rose to that temperature; a sufficient quantity of the distillate was then collected separately, while the thermometer reading remained constant, and its density and composition determined in the usual manner. The same thermometer, T_2, was used,

and the experiments were made on a day when the barometer stood at very nearly the same height as when the experiments recorded in the above table were made. Two distillations were made and fractions collected each time at 81·80°; the density of the distillate passing over at this temperature was found to be, in the first experiment, 0·85263; and in the second, 0·85254; the mean, 0·85258, corresponds with 76·32 per cent. of alcohol, which agrees well with the number 76·46, obtained in the coil. Two distillations were also made in which fractions were collected at 86·50°; their densities were found to be 0·87752 and 0·87756 respectively; the mean, 0·87754, corresponds with 65·88 per cent. of alcohol, which is exactly the quantity of alcohol contained in the distillate from the coil at the same temperature. There can therefore be no doubt that the distillate from the still-head is always identical with that from a mixture boiling at the temperature of the still-head.

A mixture of two liquids containing an indefinitely small quantity of the liquid of higher boiling point boils at a temperature but little removed from the boiling point of the more volatile substance, and emits a vapour which contains this substance only; if therefore we keep the still-head at that temperature, we ought by the law above stated to obtain a distillate consisting wholly of the more volatile substance whatever may be the composition of the mixture in the still, and thus effect a complete separation of the two liquids at one operation. In order to see whether this deduction from the law could be verified in practice, a number of distillations were made with different mixtures, the still-head being always maintained at the lowest possible temperature, which was (except in special cases) the boiling point of the more volatile substance.

Carbon Disulphide and Benzene.—In a paper previously referred to (this Journal, 1880, Trans., 59), experiments were recorded in which it was proved that a distillate containing 98 per cent. of CS_2 could be obtained even from a mixture containing only 25 per cent. of that substance.

Benzene and its Homologues.—In the same paper it was shown that practically pure benzene could be obtained from very crude material by maintaining the coil at 80·5°.

Carbon Disulphide and Carbon Tetrachloride.—Two experiments were made with mixtures of these two substances, the temperature of the still-head being as low as was compatible with a tolerably rapid distillation; when a mixture containing 63 per cent. of CS_2 was put in the still and the still-head maintained at 47·1°, the distillate was found to contain 97·3 per cent. of CS_2; with a mixture

containing 55 per cent. of CS_2, and the still-head at 47·5°, a distillate containing 95·9 per cent. of CS_2 passed over. These numbers are not the best attainable, since the temperature of the still-head in both cases considerably exceeded that at which CS_2 boils, viz., 46·5°; if, however, the temperature be allowed to approach this limit more nearly, the distillation becomes very slow, and finally almost impracticable. It should also be remembered that the above percentages are reckoned in molecules, and that the percentages of CS_2 by weight would be about 98·6 and 98·0 respectively.

Carbon Tetrachloride and Toluene.—Two distillations were made with mixtures of these substances; in the first the liquid in the still contained 70·2 per cent. of CCl_4, while the distillate obtained when the still-head was kept at 76·6° contained 98·83 per cent. of CCl_4. In the second experiment the liquid in the still contained 51·4 per cent. of CCl_4; practically no distillation took place until the temperature of the still-head was raised to 79°; between this temperature and 80°, a considerable quantity of distillate was collected, the density of which showed that it contained 96 per cent. of CCl_4; the percentages in this and in the following cases express the relative weights of the two substances, and not the relative numbers of molecules.

Benzene and Dibromethane.—In this case also two distillations were made, the first with a liquid containing 55·7 per cent. of benzene, the second with one containing 65·1 per cent. The still-head being at 80°, a considerable proportion of the liquid distilled over in each case; the densities of the distillates collected were determined, and showed that they contained 99·7 and 99·8 per cent. of benzene respectively.

The above experiments show that it is possible to obtain a liquid almost entirely free from another with which it has been mixed, by means of a still-head kept at a sufficiently low temperature; the deduction from the general law is therefore verified.

Practically the process is limited in its application, on account of the great condensation in the still-head which takes place when the mixture in the still contains a large percentage of the liquid of higher boiling point; the waste of time and fuel then becomes disproportionate to the result obtained.

All the liquid mixtures hitherto considered with regard to this question of complete separation belong to one class, each consisting of substances which mix in all proportions, and between which no combination of any kind is known to take place; among this class of mixtures there are, however, some which behave in an abnormal manner, their condition approximating apparently to that of two liquids which are in contact but do not mix. In this latter case, as is

well known, the boiling point of the mixture is much lower than that of either of the two substances (see this Journal, 1879, Trans., 547); in the same way the boiling points of many mixtures, in which one of the two liquids is an alcohol or other substance containing hydroxyl, methoxyl, or some other derivative of hydroxyl, and the other a hydrocarbon, a chlorinated hydrocarbon, or generally a substance which does not contain hydroxyl, are often lower than that of either of the constituent substances. When this is the case, it is evident that if the still-head is maintained at the boiling point of the most volatile substance, that substance will not pass over alone; on the contrary, the distillate will have the composition of the vapour evolved by that mixture, which boils at the temperature of the still-head. That such a mixture must exist is clear, when we remember that the boiling point varies continuously when the composition of the mixture varies, and that some mixtures have a lower boiling point than that of the most volatile substance.

As examples of such mixtures, we may take those of carbon disulphide and alcohol, and carbon disulphide and acetic ether.

Carbon Disulphide and Alcohol.—Pure ethyl alcohol was digested twice with quicklime, and was finally distilled from a fresh quantity of that substance; its density at 20° referred to water at 20° was then found to be 0·79322. According to Mendelejeff (*Pogg. Ann.*, **138**, 103 and 230) the density of absolute alcohol at 20° referred to water at 4° is 0·78945; referred to water at 20° this would be 0·79079, whence the above alcohol contains 0·8 per cent. of water. The number 0·79079 is taken as the true density of alcohol, while 1·26575 was that of the carbon disulphide employed. As the change of volume resulting from the mixture of alcohol and CS_2 is unknown, we must content ourselves with supposing that no such change takes place: in this case if—

x = percentage of weight of CS_2 in any mixture,
D = density of that mixture,
D_1 = density of CS_2,
D_2 = density of alcohol,

the value of x is given by the equation—

$$x = \frac{100\ D_1 (D - D_2)}{D\ (D_1 - D_2)}.$$

The cylinder surrounding the still-head having been filled with carbon disulphide boiling at the ordinary pressure, two distillations, A and B, were made.

A. The mixture in the still at the commencement of this distillation

contained 36·6 per cent. of CS_2, and at the end 2·6 per cent.; the distillate was collected in three portions, which contained respectively 87·1, 87·4, and 87·2 per cent. of CS_2.

B. In this second distillation the composition of the liquid in the still was not determined; a large fraction of the distillate which was collected contained 87·4 per cent. of CS_2.

Carbon Disulphide and Ethyl Acetate.—The ethyl acetate employed was purified by fractional distillation and dried, but it was not very pure; its density at 20° was 0·88607.

The still-head being surrounded as before with boiling CS_2, two fractions were collected which contained respectively 72·7 and 72·4 per cent. of CS_2.

These examples suffice to show the difference between the results obtained with such mixtures and those derived from the distillation of the normal mixtures, such difference arising, as was before remarked, from the fact that their vapour-tensions are higher than those of either of the constituent substances. This singular variety in mixtures which have the same outward appearance will, I hope, form the subject of a future communication.

Alcohol and Water.—When a mixture of alcohol and water is boiled in the still, and the temperature of the still-head is very gradually raised, no distillation takes place until the thermometer reaches 78°; if the still-head be then kept at this temperature, the distillate is found to be uniform in composition, and to contain 90·7 per cent. of alcohol; it is therefore impossible to obtain absolute alcohol by this process, the reason apparently being, as we shall see presently, that a spirit containing 90·7 per cent. of alcohol evolves when boiled a vapour of the same composition as itself.

We have now to endeavour to explain the various facts described above, and to understand how it is, that when a mixture of two substances is distilled, the vapour issuing from the still-head is constant in composition and contains as much of each of the two substances as does the vapour which is evolved by that mixture which boils at the temperature of the still-head. At first sight it would appear almost incredible that when a mixture of two vapours is made to pass through a tube which is just hot enough to prevent the condensation of one of them, that one and that only should issue from the other end. If a current of air be made to pass through a tube, the sides of which are wetted with benzene or any other volatile liquid, it will, as is well known, carry with it a quantity of that substance dependent on the vapour-tension of the liquid, and consequently on the temperature of the tube: why then does a current of carbon disulphide gas escape

from such a tube almost completely free from benzene? The answer to this question must, I think, be sought in the different action of the molecules of benzene upon those of air and of carbon disulphide respectively. That such a difference does exist is made manifest by the fact that mixtures of CS_2 and C_6H_6 can be made having any required boiling point between 46·5° and 80·2°, whereas it is known that no mixture of air and benzene can be obtained having a boiling point between 0° and 80°, while there is no probability that any mixtures having lower boiling points can exist. Now the absence of a series of mixtures having boiling points varying continuously from that of the more volatile to that of the less volatile substance is characteristic of two liquids which do not mix, for a mass containing two such liquids has the same boiling point whatever may be the proportion in which they are present. We may therefore presume that air and benzene, or more strictly speaking, nitrogen or oxygen and benzene, are substances which do not mix in the liquid state, and we may ascribe to this fact the different result obtained when their mixed vapours are passed through a tube.

When a mixture of two liquids which mingle in all proportions is heated to ebullition, it evolves, as we have repeatedly seen before, a mixed vapour containing a certain proportion of each of the two substances, the liquid mixture and the gaseous mixture being mutually related and existing together in a state of equilibrium. If an infinitesimally small quantity of heat be added to the mass, it will result in the formation of more of the gaseous mixture, if on the other hand, a similar quantity of heat be abstracted, the slight condensation taking place will yield an additional quantity of the liquid mixture. It is, I think, on this reciprocity between the liquid and the vapour, that depends the action of the still-head in fractional distillation.

In order to render this clear, let us imagine a mixture of two liquids, A and B, to be placed in the still, the boiling point of such mixture being θ, while the boiling point of A is t_1, that of B, t_2: let T be the temperature of the still-head, and let $t_1 < T < \theta < t_2$. As the mixed vapour evolved by the liquid in the still ascends the tube forming the still-head, its temperature will gradually sink from θ to T. Let us divide this period of cooling into n very small intervals; during the first of these the condensation of the vapour will result in the formation of a small quantity of liquid having the composition of the mixture in the still. Since the liquid mixture is in all ordinary cases poorer in A than the corresponding gaseous mixture, this condensation will leave the rest of the vapour richer in A. During the second period of cooling, this remaining gaseous mixture will be partially condensed, yielding a very small quantity of the liquid mixture to which it is related. This second period will therefore again

add to the proportion of A in the ascending vapour; the succeeding periods will do the same, and so on, until the gaseous mixture becomes identical with that evolved by a liquid mixture of which the boiling point is T, or in other words till the vapour becomes sufficiently rich in A to avoid further condensation; it then ascends the rest of the still-head unaltered, and passes into the condenser, its composition necessarily obeying the law indicated by the experiments detailed above. When $t_1 = T$, it is clear that the process of condensation and consequent enrichment in A will go on until that substance is left alone, for any gaseous mixture containing ever so little of the vapour of B will suffer partial condensation in a tube maintained at t_1.

In the case of alcohol and water, a spirit containing about 90 per cent. of alcohol distils unchanged, the vapour and the corresponding liquid having the same composition. When therefore the ascending vapour reaches this strength, any further cooling produces total condensation; the process of enrichment can go no further, and if distillation takes place at all, the distillate can contain no more than 90 per cent. of alcohol.

The cases of alcohol and carbon disulphide and of ethyl acetate and carbon disulphide, are also fully met by the above explanation.

It appears to me that this *reciprocity* between a liquid mixture and the gaseous mixture which it evolves on ebullition, has been often neglected by those who have reasoned on these and similar questions, and that the arguments which they have brought forward have often been much reduced in value by such neglect.

LXIX.—*On the Action of Oxides on Salts.* Part III.

By Edmund J. Mills, D.Sc., F.R.S., and C. W. Meanwell.

27. In pursuance of previous researches,* we directed our attention to the important cases considered below.

A. *Silica and Alkaline Sulphates.*

Sodic chloride, purified by precipitation with hydric chloride and washing with distilled water, was evaporated with hydric sulphate and ignited; towards the end of the ignition, some ammonic carbonate was added. This treatment was repeated until the last traces of chlorine were expelled. The residue, which was persistently acid to litmus, was neutralised with caustic soda freshly prepared from sodium, ignited again, powdered and sifted. It was always ignited once more before use.

In order to prepare pure potassic sulphate, we submitted the chlorate to repeated crystallisation and ignited it, first alone, then after treatment with hydric sulphate, and, lastly, after exact neutralisation with pure potassic carbonate. This salt was always treated before use, in the same manner as the sodic sulphate. The silica was part of the stock referred to in previous memoirs.

Five grams of either of the sulphates were now mixed with 1 gram of silica, in a small platinum crucible, which was enclosed by another of the same material, and kept from actual contact with it by a few fibres of asbestos. To this arrangement heat was applied by means of a Fletcher's burner for periods of three hours; at first very gently, but afterwards very intensely, and with the aid of a draught. In another series of experiments the outer crucible was removed, and the highest temperature again resorted to. In the first series, the outer crucible was of glazed porcelain.

28. Throughout these experiments we invariably observed either that the mixture underwent no change of weight, or that, in the event of its doing so, the platinum was attacked, and a soluble alkaline sulphide produced. We accordingly infer that at all temperatures up to bright redness at least, pure silica is without action on potassic or sodic sulphate.

This remarkable result, to ourselves wholly unexpected, induced us to try the action of alumina upon the sodic sulphate.

* For Part II, see Journal (1879) i, p. 336.

University of Michigan

B. *Alumina and Sodic Sulphate.*

29. The sodic sulphate was a portion of the sample used in the experiments with silica.

The alumina was prepared as follows:—Some potash alum, which gave no reaction with potassic ferrocyanide, and in which we failed to detect any other impurity having influence on our work, was dissolved in a large quantity of distilled water, and to this rather more ammonia was added than would be sufficient for complete precipitation. After washing by decantation until soluble sulphate was no longer present, the precipitate was dissolved in pure hydric chloride, again thrown down with ammonia, and washed as before. It was then dried at 100° and strongly ignited in a platinum crucible enclosed within an earthen one; the fuel used being paraffin still coke, which is free from sulphur and ash.

In carrying out the experiments, a constant weight of sulphate (1·5 gram) was mixed in a small platinum crucible, with varied weights of one sample of alumina, thus prepared. The crucible was placed in a platinum saucer, from which it was separated by a few fibres of asbestos; the object of the saucer being to prevent as far as possible the intrusion into the crucible of reducing gases. Beneath the saucer, at a suitable distance, was a specially constructed blowpipe. Coal-gas was supplied to this instrument through a cone regulator, and air from an injector driven by a water-supply at constant pressure through an elastic bag. Every effort was thus made to maintain constant conditions. The temperature was that of light redness, and the duration of incandescence six hours.

30. We now always encountered, without the formation of sulphide, an appreciable amount of chemical change, this being indicated both by the loss of weight and the alkaline reaction of the mixture. Our results are comprised in the following table:—

TABLE X.

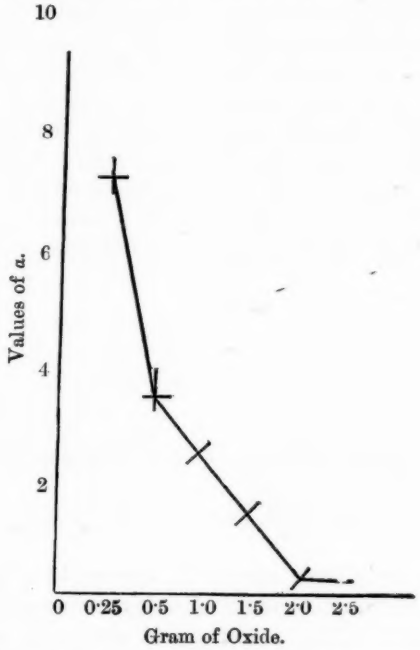
Gram of alumina.	x.	Gram of sulph. oxide expelled.	e.	Remaining sulphate.	y_r	a.
0·25	·0024529	·1649	·0020625	1·2071	·0085001	8·7190
0·50	·0049056	·1257	·0015722	1·2767	·0089904	4·1201
1·00	·0098115	·1201	·0015022	1·2867	·0090604	2·7354
1·50	·014718	·0762	·00095310	1·3647	·0096095	1·4194
2·00	·019623	·0155	·00019387	1·4725	·0103688	0·28051
2·50	·024529	·0156	·00019512	1·4723	·0103675	0·26280

In order to convert grams into chemical units, we have used $Al_2O_3 = 101{\cdot}92$, $Na_2SO_4 = 142{\cdot}01$, and $SO_3 = 79{\cdot}95$ as divisors.

31. If e represent chemical effect, measured by units of sulphuric anhydride, expelled, x the alumina taken, y the sulphate employed, y_r the residual sulphate (all similarly measured), and α be the factor of condition, then, in accordance with the usual formula—

$$e = \frac{\alpha x y}{x + y_r}.$$

We have calculated the values of α, which are not constant, and have given a list of them in the table. In the accompanying figure, we have graphically represented them as a function of x.



In this figure it at once becomes apparent that the action of alumina is most energetic when a comparatively small mass of the oxide is used. There are, moreover, three distinct stages in the action. In the first, the value of α clearly takes the form $(A - \mu B)$, B being the number of grams of alumina; but we are unable to assign the values of A and μ. In the second, α is also linear, and proves to have the value—

$$\alpha = 4{\cdot}1200 - 2{\cdot}67\ (B - 0{\cdot}5).$$

In the third stage, α is sensibly constant and equal to 0·27166.

The maximum value of x in the second stage is obtained by putting $\alpha = 1 = 4{\cdot}1200 - 2{\cdot}67\ (B - 0{\cdot}5)$, whence $B = 1{\cdot}67$ gram. The figure in fact shows that this point must lie somewhat beyond 1·50 gram.

At first, then, the action of alumina upon sodic sulphate is such as to give rise to a polysodic aluminate or polysodic aluminates of very high order; this kind of action diminishing until $3Al_2O_3$ approximately expel SO_3. In like manner the second stage terminates nearly, when $100Al_2O_3$ expel SO_3; and in the third stage a still greater effort is required. It is also evident that beyond about $126Al_2O_3$, the further addition of alumina produces no useful effect.

32. In Part II, where the action of ferric oxide on potassic carbonate was described, it was pointed out that there are three stages also in that action. Of these the first exactly resembles the first stage of the action of alumina on sodic sulphate; in the second, however, α is constant, while in the present case it diminishes linearly with the weight of oxide; in the third stage, it is in each case constant. On the other hand, when alumina acts on potassic carbonate, the factor of chemical effect undergoes linear increase with the mass of the oxide. The behaviour of an oxide with a salt is thus demonstrated to depend both on the oxide and the salt; so that no general inference can be drawn, in the comparison of a pair of oxides, from their deportment with a single salt.

LXX.—*On the Action of Tertiary Amines upon Acetylene Dibromide.*

By R. T. Plimpton, Ph.D.

It appeared possible that acetylene dibromide might react with tertiary amines, forming bromides of ammonium bases containing the unsaturated group $(C_2H_2)''$, and either analogous to the ethylene compound, $N(C_2H_5)_3(C_2H_4Br)Br$, of Hofmann, or simple addition compounds of the formula $BrR_3N{-}CH{=}CH{-}NR_3Br$. Some experiments which I have made with trimethylamine and triethylamine show, however, that a more complicated reaction takes place, giving rise to the formation of bromides of the corresponding ammonium bases, hydrobromides of the tertiary and secondary amines, and dark substances containing the carbon of the acetylene. The acetylene dibromide used for the following experiments was prepared by treating the tetrabromide in alcoholic solution with zinc powder (Sabanejeff, (*Ber.*, **9**, 1441). It boiled at 110—111°, and did not solidify at

— 17°. Its specific gravity was found to be at 0° = 2·268. A bromine determination gave Br = 85·81; theory 86·02.

Trimethylamine.

The acetylene dibromide was heated with an alcoholic solution of trimethylamine (2 mols.) for two days at 115—120°. On cooling, the tubes were found to contain considerable quantities of a crystalline bromide, and the liquid, which had become dark-coloured, held in solution unaltered bromide and trimethylamine. No gas was formed in the reaction. The crystals, after treatment with animal charcoal and recrystallisation from weak alcohol, gave on analysis Br = 51·74, 51·99; calculated for tetramethylammonium bromide 51·94. The platinochloride crystallised from hot water in octohedrons, and gave on analysis Pt = 34·94, calculated 35·18; C = 17·7, H = 4·6; calculated C = 17·3, H = 4·3.

The dark-brown mother-liquor was evaporated on the water-bath, and the resulting deliquescent crystalline mass treated with water, which separated a small quantity of a brown amorphous substance. The filtrate was then treated with silver oxide, by means of which a further quantity of a similar substance was removed, together with the bromide of silver, and neutralised with hydrochloric acid. Addition of a small quantity of platinic chloride produced a precipitate which contained the remainder of the colouring matter, together with a very small quantity of a platinum salt, probably that of tetramethylammonium. From the filtrate on evaporation a platinum salt was obtained crystallising in needles. Analysis gave Pt = 39·32, 39·42, and 39·14; calculated for dimethylamine platinochloride 39·12.

In some other experiments the brown mother-liquor of the tetramethylammonium bromide was evaporated, and the residue distilled with potash. The distillate was found to contain a mixture of di- and tri-methylamine.

Triethylamine.

Acetylene dibromide was heated with triethylamine (2 mols.) in alcoholic solution for 20 hours at 105°. On cooling, the tube was found to contain a quantity of crystals which were separated from the brown mother-liquor, dissolved in alcohol, and precipitated with ether. A bromine estimation showed them to be triethylamine hydrobromide. Found Br = 43·62; calculated 43·95.

The brown mother-liquor contained unaltered bromide and triethylamine, and was therefore again heated in a sealed tube. Even after heating for 48 hours at 105° the reaction was not complete, and on distilling off part of the alcohol small quantities of the unaltered sub-

stances passed over. A second quantity of crystals which separated out on cooling proved to be a mixture of diethylamine hydrobromide and tetrethylammonium bromide. The mother-liquor was then evaporated, the residue dissolved in water, filtered from some dark substance, and treated with silver oxide. On distilling the solution diethylamine passed over. It was converted into the platinum salt, which gave on analysis Pt = 35·3; calculated 35·2.

The solution of the hydrates was neutralised with hydrochloric acid, and fractionally precipitated with platinic chloride. Eight precipitates were obtained, of which the first two contained some colouring matter. Platinum estimations made with Nos. 2 and 8 gave Pt = 29·1; calculated for tetrethylammonium platinochloride 29·3.

Triethylamine therefore reacts on acetylene dibromide in the same manner as trimethylamine, with formation of tetrethylammonium bromide, triethylamine and diethylamine hydrobromides, and carbonaceous bodies.

These experiments were made in the laboratory of University College, London.

LXXI.—*Suberone.*

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

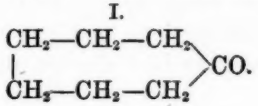
In our last communication we stated that the investigation of this interesting compound would be continued (*Chem. Soc. J.*, 1879, **1**, 684). We first tried to combine it with nascent hydrogen, but without success. By acting on it with phosphorus pentachloride, a heavy liquid chloride was obtained, which could be distilled with steam. On dissolving it in alcohol and adding sodium, it was converted into a hydrocarbon which readily combined with bromine. As the quantity of suberone at our disposal was not very large, and the conversion of it into volatile hydrocarbon could not have been effected without great loss of our precious material, we intended to work in another direction, but pressure of other work prevented us from continuing this research.

We were therefore very glad when our friend Dr. A. Spiegel, who assisted us in our former investigation, made the offer to work the subject out for us. The results which he obtained are described in the following. He worked quite independently, and the only part which we took in this research was to provide him with the material.

In order to establish the constitution of suberone, it appeared desirable to ascertain first that of suberic acid, which is a dicarboxylic acid of normal hexane. On converting it into suberone and oxidising the latter, α-pimelic acid is formed, or a dicarboxylic acid of normal pentane. From this it follows that one carboxyl of suberic acid is in the primary position, which may also be the case for the second; but it is also possible that the latter occupies a secondary position, and if so, suberic acid ought to be converted into hydroxysuberic acid by oxidising it with potassium permanganate in an alkaline solution: for the experiments of R. Meyer (*Ber.*, **11**, 1787) and others have shown that this conversion of hydrogen into hydroxyl appears to take place only when the formation of hydroxyl gives rise to a tertiary compound. It was, however, found that permanganate acts so energetically and the quantity required is so large, that a complete combustion had doubtless taken place.

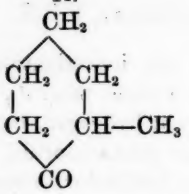
If suberic acid contains the two carboxyls in primary position, suberone would contain a ring of seven carbon-atoms, or its constitution would be expressed by the following formulæ:—

I.

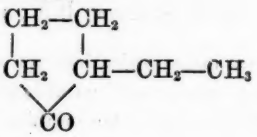


In the case that only one hydroxyl occupies the primary position, we have a choice among the following formulæ:—

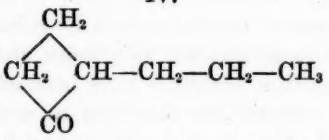
II.



III.



IV.



All such compounds would yield α-pimelic acid on oxidation, the ring being broken and the carbon being converted into carboxyl, whilst the second carboxyl would be furnished in the first case by the oxidation of CH_2, and in the three latter by the methyl-group. Formula I, however, appears not probable; as far as our experience goes, no more than 6 atoms of carbon can be linked together to form an annular chain.

The presence of carboxyl being the cause of the easy rupture of the chain, it was next tried to remove the oxygen in order to ascertain how many carbon-atoms are contained in the ring. This was effected in the following way. Suberone readily combines with hydrocyanic acid in the nascent state, yielding the cyanhydrin $C_7H_2(OH)CN$, which is a colourless liquid. On bringing it in contact with concentrated hydrochloric acid, heat is developed, sal-ammoniac separates out, and the whole very soon solidifies. Water was now added, and the unaltered suberone distilled off with steam. The residue was made alkaline and shaken with ether, which removed two neutral compounds. One of these is insoluble in water, and crystallises from alcohol in colourless needles melting at 179°; the second crystallises from hot water in pearly plates melting at 130°.

After these bodies had been completely removed, the liquid was acidified and again treated with ether, to isolate the new acid, which may be called *hydroxysuberancarboxylic acid* or *suberylglycollic acid*, $C_7H_{12}(OH)CO_2H$. It was purified by repeated crystallisation from benzene and hot water; from the latter it separates in glistening narrow plates, being often an inch long, and containing half a molecule of water, which they lose in a vacuum over sulphuric acid, or at 60°.

(1.) 0·2542 lost over sulphuric acid 0·0120.
(2.) 0·4230 lost at 60° 0·0212.

Calculated for $2C_8H_{14}O_3 + H_2O$.	Found.	
	(1.)	(2.)
5·11 per cent.	4·72	5·01

The hydrated acid melts at about 50°, whilst after the water has been expelled, the melting point is 79—80°; on heating it more strongly it volatilises slowly. It tastes sweetish at first, then strongly astringent, like alum; dissolves freely in alcohol, ether, chloroform, hot water, and hot benzene, crystallising from the latter in anhydrous glistening needles, which gave on analysis the following results:—

	Substance.	CO_2.	H_2O.
(1.)	0·1626	0·3623	0·1305
(2.)	0·1564	0·3462	0·1258

	Calculated.		Found.	
			(1.)	(2.)
C_8	96	60·76	60·76	60·37
H_{14}.....	14	8·86	8·91	8·93
O_3	48	30·38	—	—
	158	100·00		

On heating the acid with concentrated hydrochloric acid to 120—130°, it is converted into *chlorsuberancarboxylic acid*, $C_7H_{12}Cl.CO_2H$, which is isolated by diluting the product with water and exhausting with ether. It is a thick, colourless liquid, which does not solidify on standing, and produces a burning pain on the skin. Alcohol, ether, and benzene dissolve it freely, but it is insoluble in water. On dissolving it in a little ammonia, the ammonium salt soon crystallises in pearly plates.

By the action of alcoholic potash, or by boiling with caustic soda, the chlorinated acid is converted into *suberancarboxylic acid*, $C_7H_{11}.CO_2H$, which dissolves very readily in alcohol, ether, chloroform, and benzene, and volatilises with steam, being deposited in the condenser in pearly plates, melting at 53—54°. It combines with bromine, and the crystalline product thus formed loses by treatment with alcoholic potash the elements of hydrobromic acid, a new acid being formed, which has not been further investigated.

On adding sodium-amalgam to an aqueous solution of suberencarboxylic acid, it takes up hydrogen, and is converted into *suberancarboxylic acid*, $C_7H_{13}.CO_2H$, a colourless liquid, which can be distilled with steam, and has the smell of fatty acids.

This compound is derived from suberone by the conversion of CO into $CH.CO_2H$, the carbonyl being not only completely reduced, but its position also being marked by the carboxyl-group. It was to be expected that if this acid contains an alcohol-radical as side-chain, the latter would by oxidation be converted into carboxyl, a bibasic acid being formed. The presence of a tertiary carbon-atom excluded the employment of potassium permanganate. It was therefore dissolved in common nitric acid, and the solution boiled in a flask connected with a reversed condenser, until the evolution of nitrous fumes ceased, which was the case after two days' heating. On the addition of water, no suberancarboxylic acid separated out, and on evaporating the solution, a syrupy residue was obtained, from which on standing granular crystals were deposited, which were purified by repeated crystallisation. The new acid thus obtained forms compact crystals, melting at about 100°, being readily soluble in water, and having a strongly acid taste. From the following analysis of its silver salt it appears that it is a bibasic acid, having the composition $C_8H_{12}O_4$, or $C_8H_{14}O_4$—

0·0640 left on ignition 0·0370 silver.

Calculated.		
$C_8H_{10}O_4Ag_2$.	$C_8H_{12}O_4Ag_2$.	Found.
58·12 p. c. Ag.	57·84	57·81

The further examination of this characteristic and well-defined acid will undoubtedly throw much light on the constitution of suberone, but must be postponed until we have again procured a sufficient quantity of this expensive material.

These imperfect results gain in interest by another observation. When suberglycollic acid is heated with concentrated sulphuric acid, torrents of sulphur dioxide escape, and the solution, which assumes only a slightly brown colour, contains, according to the time of heating, either an acid which dissolves freely in water, or one which is almost insoluble. This behaviour of the glycollic acid reminds one of that of hydromellitic acid, $C_6H_6(CO_2H)_6$, which is thus converted into the two isomerides, $C_6H_2(CO_2H)_4$, prehnitic and mellophanic acid, and by the same reaction piperidine, $C_5H_{11}N$, is oxidised to picoline, C_5H_5N (Koenigs, *Ber.*, **12**, 2341). This reaction will also be more fully studied, as soon as possible.

LXXII.—*On Dimethylmalonic Acid and Dimethylbarbituric Acid.*

By L. T. Thorne, Ph.D.

By the action of methylic iodide on the di-argentic derivative of barbituric acid ($C_4Ag_2H_2N_2O_3$) Conrad and Guthzeit (*Ber.*, **14**, 1643) obtained a di-methylbarbituric acid, which, however, differed in properties from that which Mulder obtained (*Ber.*, **12**, 466) by acting on a mixture of malonic acid and phosphoric chloride, with dimethylurea.

To determine the constitution of their substance, Conrad and Guthzeit saponified it with a strong solution of potassic hydrate. Ammonia was evolved, and on acidifying the alkaline residue and extracting with ether, an acid was obtained fusing at 185°, and giving analytical results corresponding to dimethylmalonic acid. Markownikoff, however, who first prepared this acid by the action of potassic cyanide on bromisobutyric acid, and decomposition of the resulting product with hydrochloric acid (*Ann.*, **182**, 336), gives its melting point as 170°. In order to explain this discrepancy, I determined to prepare dimethylmalonic acid by the method described by Conrad (*Ann. Chem.*, **204**, 129) for preparing substituted malonic ethers.

48 grams of ethylic malonate were mixed with a 9 per cent. alcoholic solution of sodic ethylate containing 6·3 grams of sodium, 50 grams of methylic iodide gradually added to the cooled mixture, and the whole then heated on a water-bath until neutral. 6·3 grams of sodium, in the form of sodic ethylate, and 50 grams of methylic iodide were then again added, and the whole further heated until it no longer showed an alkaline reaction. After the addition of water the ether was separated, washed, dried, and distilled. The greater part passed over between 193° and 195°, and on fractioning, the boiling point was found to be 194·5°.

0·1131 gram of substance gave, on combustion, 0·0886 gram H_2O, and 0·2357 gram CO_2.

	Calculated for $C_9H_{16}O_4$.	Found.
C_9	57·44	56·84
H_{16}	8·51	8·70
O_4	34·05	—

Ethylic dimethylmalonate, $C(CH_3)_2(COOC_2H_5)_2$, is a colourless mobile liquid of

pleasant odour. Its sp. gr. at 25° is 0·9965 as compared with water at 15°, and its boiling point is 194·5°.*

The acid was prepared by saponifying the ether with caustic potash, to which about one-half its own weight of water had been added, neutralising, washing with ether to remove undecomposed traces of the original ether, acidulating, and extracting the liberated acid with ether. On evaporation of the etheric solution, a crystalline mass was left, which after several recrystallisations from water and ether, fused constantly, but always with partial decomposition, at 186°.

I. 0·1565 gram acid gave 0·0861 gram H_2O and 0·2579 gram CO_2.
II. 0·1130 „ „ 0·0643 „ H_2O „ 0·1866 „ CO_2.

	Theory for $C_5H_8O_4$.	Found. I.	Found. II.
C_5	45·45	44·94	45·04
H_8	6·06	6·11	6·32
O_4	48·49	—	—

Dimethylmalonic acid crystallises in colourless monoclinic pyramids, which are often truncated. It melts at 186°, but sublimes long before its point of fusion. Sublimation commences at a little over 100°, but is very slight below 170°, and cannot be used for purifying the acid, as partial decomposition into carbonic and isobutyric acids sets in at about 130°. At the fusing point decomposition takes place very rapidly. The sublimed acid condenses in monoclinic prisms usually grouped together into feathery shapes. The acid is very soluble in water and ether, moderately so in alcohol.

Zincous dimethylmalonate was prepared by adding pure zincous carbonate to a weak boiling solution of the acid. On slow evaporation at 100°, the zinc salt crystallised out in monoclinic pyramids.

I. 0·2947 gram salt gave 0·1002 gram H_2O, and 0·3008 gram CO_2.
II. 0·1674 gram salt gave 0·0562 gram H_2O, and 0·1705 gram CO_2.
III. 0·1618 gram salt gave 0·0608 gram ZnO.

	Theory for $ZnC_5H_6O_4$ + Aq.	Found. I.	Found. II.	Found. III.
C	28·17	27·84	27·77	—
H	3·75	3·78	3·73	—
Zn	30·52	—	—	30·15
O	37·56	—	—	—

The zinc salt crystallises therefore with 1 molecule of water, and

* The lowering effect produced on the boiling point of homologous substances by the increase of methyl groups in the radical is very marked here. The ether of dimethylmalonic acid boils half a degree below that of malonic acid.

this it does not give up below about 150°, and then only with partial decomposition of the salt. A determination of its solubility gave the following results. Two portions, each of 25 c.c. of solution filtered at 24°, left on evaporation and drying by 120° residues of 0·1695 and 0·1696 gram respectively. This represents 0·6780 respectively. 0·6784 gram of hydrated salt in 100 c.c. of solution, or 1 part of salt is soluble in 147 parts of water at 24°. Markownikoff describes his zinc salt as crystallising with 3 mols. of H_2O, and being soluble in 106 parts of water.

Dimethyl-malonamide was obtained by heating ethylic dimethyl-malonate in closed tubes to 120° with a large excess of a saturated alcoholic solution of ammonia. The yield was, however, very small. The amide crystallises in needles, which melt at 196—198°, and on resolidifying do not again fuse till 208—210°, probably owing to conversion into the imide. A nitrogen estimation was made by boiling the amide with potassic hydrate, and titrating the evolved ammonia.

The ammonia produced from 0·1365 gram amide neutralised 2·14 c.c. normal H_2SO_4, corresponding to 21·94 per cent. of nitrogen. The formula $C_5H_{10}N_2O_2$ requires 21·54 per cent. nitrogen.

Thus it is clear that the acid obtained by Markownikoff could not have been pure, and this is easily accounted for by the inconvenient way in which he had to prepare it. The intermediate cyanoisobutyric acid was not obtained in a state of purity, and Markownikoff does not give a single analysis in his paper to prove the purity of his dimethylmalonic acid or its salts.

To remove all doubt of the correctness of the constitution ascribed to their dimethyl-barbituric acid by Conrad and Guthzeit, I further prepared this substance from dimethylmalonic acid and urea in a similar manner to that recommended by Grimaux (*Ber.*, **12**, 378) for the preparation of barbituric acid. The reaction takes place according to the following reaction :—

$$3\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}COOH\\COOH\end{matrix} + 3CO\!<\!\begin{matrix}NH_2\\NH_2\end{matrix} + 2POCl_3$$

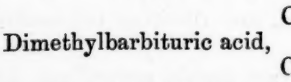
$$= 3\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CO—NH\\CO—NH\end{matrix}\!>\!CO + 6HCl + 2H_3PO_4.$$

2·5 grams of dimethylmalonic acid were intimately mixed with 2·5 grams of urea and 2 grams of phosphoric oxychloride added. The reaction commenced in the cold, but before it was completed the mixture required to be heated for several hours on a water-bath. The nearly solid mass was then treated with a little *cold* water, and the residue dissolved in a small quantity of boiling water. This solution on cooling deposited the greater part of the acid in the form of

glistening scales, which after several recrystallisations were obtained almost colourless. When heated very slowly, this substance sublimed without melting, and condensed again in the form of minute colourless needles. The nitrogen was determined by Zulkowski's modification (*Ann. Chem.*, **186**, 296; *Ber.*, **13**, 1096) of Dumas' method.

I. 0·1388 gram acid gave 0·0677 gram H_2O and 0·2340 gram CO_2.
II. 0·1961 „ gave 28·0 c.c. N at 24° F., and 756·7 mm. bar. (corr.).

	Theory for $C_6H_8N_2O_3$.	Found. I.	Found. II.
C	46·15	45·98	—
H	5·13	5·42	—
N	17·95	—	18·47
O	30·77	—	—

Dimethylbarbituric acid,  , melts without decomposition at 265°, but sublimes far below that temperature; it is very slightly soluble in cold, much more so in boiling water, and agrees in all respects with that described by Conrad and Guthzeit.

There can therefore be no doubt that, as pointed out by those chemists, the first two hydrogen-atoms replaced in barbituric acid, in the formation of its salts, are those contained in the CH_2 group of the malonyl-radical, and not, as hitherto believed, those attached to the two nitrogen-atoms. It is only after the replacement of the former that the latter become capable of displacement.

I take this opportunity to thank Professor M. Conrad, of Aschaffenburg, in whose laboratory this research was carried out, for his kindly interest and advice during that time.

LXXIII.—*On Phenylnaphthalene.*

By Watson Smith, Demonstrator and Assistant Lecturer in Chemistry in the Owens College, and T. Takamatsu.

The chief object of this research was to find a means of increasing the yield of phenylnaphthalene, for the first time synthetically obtained by one of us in 1879 (*Ber.*, **12**, 1396 and 2049). The same materials were used as before, viz., a mixture of bromobenzene and naphthalene, but a larger furnace was used, so that an increased

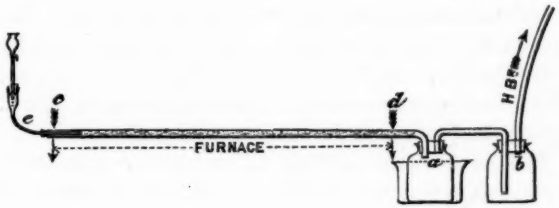
length of heated surface could be employed. The furnace was an Erlenmeyer's gas-combustion furnace with thirty burners; it was obtained from Rohrbeck of Berlin.

The details and results are as follows:—

According to the reaction—

$$\underset{\text{Bromobenzene.}}{C_6H_5Br} + \underset{\text{Naphthalene.}}{C_{10}H_8} = \underset{\text{Phenylnaphthalene.}}{C_6H_5.C_{10}H_7} + HBr,$$

157 parts of bromobenzene require 128 parts of naphthalene. Over 300 grams of the latter were taken and dissolved, with the aid of heat, in 300 grams of the former, and the warm liquid was poured into a tap-funnel connected with a bent tube passing slantwise into the combustion-tube, the latter at a bright red heat in the furnace. The excess of naphthalene is more favourable to a good yield of the desired hydrocarbon, as already proved (*Ber.*, **12**, 2051).



The combustion-tube was of $\frac{1}{2}$-inch internal diameter, and was loosely filled with fragments of pumice-stone. After a distillation of the entire mixture, the products found in (*a*) and (*b*) fuming strongly with hydrobromic acid and quite black, were transferred to a retort and distilled to recover the unaltered bromobenzene and naphthalene. These, received over in mixture, were mingled with a little more naphthalene, and the mixture was melted and again passed through the tube. The operation was continued till all bromobenzene was exhausted. The furnace was always considerably inclined downwards from *c* to *d*, the small tube *e* being further inclined to cause the mixture to flow readily into the combustion-tube.

By thus employing a large furnace, and a more extended surface at a bright red heat, naphthalene being always maintained in excess of the quantity calculated for the reaction shown in the equation, a considerably increased yield of phenylnaphthalene was obtained, with a parallel increase of isodinaphthyl, but only very little diphenyl could be detected. The black tarry-looking stuff which had been accumulated, was now melted and poured into a retort, and submitted to distillation.

Below 200° a very little bromobenzene passed over; between 200°

and 220° undecomposed naphthalene; and when the temperature rose to 250—280°, yellowish-red oils came over, and were collected separately. At a temperature above 360°, a yellowish-brown substance distilled over, solidifying immediately to a mass of the same colour. In the retort a mass was left chiefly consisting of coke.

The oils collected between 250° and 280° solidified on cooling to a waxy mass. This and the solid portion boiling over 360°, were crushed together in a mortar with petroleum-spirit boiling between 60° and 100°; the thin fluid mass was then thrown on the filter, and after draining completely, was submitted to a fresh trituration with cold petroleum spirit.

Thus resinous matter, together with a little phenylnaphthalene, were dissolved out, yielding a red solution. The highest-boiling bright yellow and red hydrocarbons appearing last, just before coking the crude substance in the retort, appear to be identical with the precisely similar bodies appearing at the same stage in the preparation of isodinaphthyl, and also in the distillation of coal-tar immediately before the still is coked. The mass, washed as above with petroleum spirit, was dried in the water-bath, and then boiled with spirits of wine in excess, which had been previously diluted with water. In such a hot solution phenylnaphthalene is soluble, whilst dinaphthyl is quite insoluble. The solution was quickly filtered off (on a hot water funnel) from the residue, which was washed again with more hot dilute alcohol. The filtrate gave on cooling a beautiful white precipitate of phenylnaphthalene, which was collected on a filter and dried over sulphuric acid. A certain quantity of this hydrocarbon was also recovered from the petroleum-spirit washings, by repeated fractional distillations, and purifying with dilute alcohol as before.

The precipitate, when dried as above mentioned, was a white crystalline powder, with a melting point of 95—98°. It was purified by sublimation. Owing to the low melting point of the crude substance, it was at first found difficult to obtain expeditiously the pure substance by the sublimation of the crude.

A method was now devised by which a large yield of beautifully sublimed hydrocarbon could be most expeditiously obtained from the crude substance. The old form of apparatus used was an inverted glass funnel placed over a watch-glass containing some of the crude substance, the rim of the funnel standing on some smoothly laid asbestos which had been strewed on a piece of wire gauze, a small circular hole being left bare to the wire gauze through the asbestos, immediately under the centre of the watch-glass. Under the wire gauze, and immediately beneath the bare circular place left under the watch-glass, a very small Bunsen flame was lighted. In subliming crude phenylnaphthalene, or in fact any low-melting bodies with this

apparatus, or with others similarly constructed, great watchfulness is needed to prevent too great heat from remelting the lowest layers of sublimed crystals on the inner side of the funnel, thus undoing much of what had been at first accomplished. This difficulty, and the loss of time consequent upon it, were overcome by the adoption of a simple device. About a yard or so of rather less than $\frac{1}{4}$-inch block-tin tubing was procured, and this was wound most closely and accurately round the outside of the funnel to be used. Thus a conical coil was obtained, in which the funnel easily fitted and could be withdrawn at pleasure. All that was now necessary was to connect the coil at (*a*) with a cold water supply, (*b*) being the exit. A small plug of filter-paper is loosely fitted into the end of the funnel (*c*), and the whole arrangement placed as already described above. By thus cooling the outside of the funnel, a higher temperature may be employed below the watch-glass, and with great rapidity the inside of the funnel becomes filled with a beautifully sublimed mass of crystals. The sublimed phenylnaphthalene consisted of thin beautifully white plates, exhibiting a delicate blue fluorescence, though not so much as in the case of pure anthracene for example. The melting point was found to be 101—102° (corrected), whereas before sublimation it was 95—98°. The former melting point thus differs slightly from that previously found by one of us (*Ber.*, **12**, 2051). This we attribute to the fact that we had a larger quantity of substance to work upon, and our sublimation process was very much improved, thus yielding us much better and purer crystals. The delicate orange-like odour of the vapours of the hydrocarbon and other properties (easy solubility in quite dilute spirit of wine) were sufficient tests of its identity so far. A vapour-density determination by Victor Meyer's method, employing a lead-bath and an atmosphere of nitrogen, gave the following results:—

Substance taken	0·1105 gram.
Temperature	17·5° C.
Volume	13·2 c.c.
Barometer	754·1 mm.
Tension of aqueous vapour at $t°$	14·882 mm.

Hence $\frac{0{\cdot}1105(1 + 0{\cdot}003665 \times 175) \times 587780}{13{\cdot}2(754{\cdot}1 - 14{\cdot}882)} = 7{\cdot}08$ vap. density,

calculated for $\begin{matrix} C_{10}H_7 \\ | \\ C_6H_5 \end{matrix} = 7{\cdot}07.$

	Found.	Calculated.
Vapour density	7·08	7·07

A combustion gave the following numbers and result—

Substance taken = 0·1310 gram. CO_2 found = 0·4505 gram. H_2O found = 0·0705 gram.

	Found.	Calculated.
Carbon	93·78 per cent.	94·12 per cent.
Hydrogen	5·98 „	5·88 „
	99·76 „	100·00 „

The hydrocarbon dissolved in carbon bisulphide and treated with bromine, is gradually converted into a substitution-product, with evolution of hydrobromic acid. Treated with concentrated sulphuric acid it dissolves on gently warming, forming a sulphonic acid. These products will be further examined as soon as a new yield of material is obtained. The chief difficulty still in the way is the want of a more productive method of preparation—this it is hoped will also be overcome.

Addendum.

In order if possible to ascertain the isomeric position of phenylnaphthalene, we attempted to synthesize the α-phenylnaphthylene by employing Fittig's reaction. For this purpose a mixture in the correct proportions was made of monobromobenzene and monobromonaphthalene, and this mixture, after dilution with benzene, was treated with bright freshly cut slips of metallic sodium. The sodium was employed in excess, and the whole was left for five or six hours, when the reaction was aided by application of heat, until the benzene began to boil. The flask was connected with an inverted condenser, and the boiling continued for about seven hours.

It was now observed that a chocolate-coloured substance had accumulated in the flask, and covered the pieces of sodium which remained. The contents of the flask were now thrown on a filter, and the remaining particles of sodium were mechanically removed from the residue, which was then examined. In this residue we succeeded only in detecting the presence of diphenyl, and the polymeric dinaphthyl of chocolate-brown colour and amorphous structure described by Lossen. We could discover none of Lossen's dinaphthyl ($\alpha\alpha$), and certainly no trace of any new hydrocarbon. This reaction then failed in our hands, and under the circumstances detailed, to yield phenylnaphthalene. We also varied our conditions, at one time using more dilute solutions in benzene, and at another greater concentration; but in all cases our efforts were defeated by the great ease with which the chocolate-coloured substance is formed, which from its reaction and appearance, appears to be quite identical with the body described by Lossen. On

collecting a considerable quantity of the brown product of the above reaction, having first carefully separated from it any remaining particles of sodium, and placing it in a small retort and distilling, a small quantity of oils was obtained at a temperature between 250° and 350°. These oils had a peculiar unpleasant odour, and no crystalline substance could be isolated from them. In appearance, odour, and boiling point they reminded one very much of the oily products obtained by one of us on attempting to synthesize phenylnaphthalene by passing a mixture of bromonaphthalene and benzene through a red-hot tube.

LXXIV.—*Sulphonic Acids derived from Isodinaphthyl (ββ-Dinaphthyl).*

By Watson Smith, Demonstrator and Assistant Lecturer in Chemistry in the Owens College, and T. Takamatsu.

Dinaphthyl(ββ)-monosulphonic Acid, $C_{10}H_7.C_{10}H_6.SO_2OH$.—15 grams of isodinaphthyl were heated with 3 grams of concentrated pure sulphuric acid in a small flask at 200° in the oil-bath for 5—6 hours. At that temperature the hydrocarbon melted easily with the acid, forming a dark-coloured oily liquid which, on cooling, solidified to a hard mass. After the 5—6 hours' heating, the mass was on cooling treated with boiling water several times, whereby it was in greatest part dissolved. Still a residue remained, and no inconsiderable one. The mixture, without filtering, was now neutralised with pure calcium carbonate, whereby the calcium salt of the sulphonic acid in question was obtained. The liquid was now filtered in the cold. The clear filtrate was evaporated down on a water-bath, whereby only a very small residue was obtained, too little for analysis. The insoluble residue (in the cold) remaining on the filter was now transferred to a flask and boiled up with water for 20 to 30 minutes. On filtering at the boiling heat, employing a hot-water funnel, a clear filtrate was obtained, which, on cooling, deposited a snow-white crystalline precipitate. This, on examination with a lens, was seen to consist of an aggregation of small white needles. The residue on the filter was now repeatedly boiled with water, until the cooled filtrate deposited no more crystalline precipitate.

The precipitate was now collected, and washed first with cold water and afterwards with dilute acetic acid, to remove any possible con-

tamination due to the presence of calcium carbonate. After a final washing with water, it was dried over sulphuric acid in a vacuum.

Analyses of the dried calcium salt thus obtained gave the following results:—

A weighed quantity was heated in the air-bath at 150—200°, till a constant weight was obtained. The residue was then ignited with a few drops of pure sulphuric acid, and the weight of the resulting $CaSO_4$ determined.

(I.) Weight of salt taken..... 0·1490 gram.
Loss on heating at 150—200°.. 0·0080 „ = 5·37 p. c. H_2O.
$CaSO_4$ obtained..... 0·0265 „ = 5·17 „ Ca.

(II.) Weight of salt taken..... 0·1620 gram.
Loss on heating at 150—200°.. 0·0085 „ = 5·24 p. c. H_2O.
$CaSO_4$ obtained..... 0·0305 „ = 5·53 „ Ca.

	I.	II.	Mean.	Calculated for $\frac{C_{10}H_7.C_{10}H_6.SO_3}{C_{10}H_7.C_{10}H_6.SO_3}>Ca + 2H_2O$.
Ca	5·17 p. c.	5·53 p. c.	5·35 p. c.	5·30 p. c.
H_2O....	5·37 „	5·24 „	5·30 „	4·86 „

Calcium Dinaphthyl(ββ)monosulphonate, $\frac{C_{10}H_7.C_{10}H_6.SO_3}{C_{10}H_7.C_{10}H_6.SO_3}>Ca+2H_2O$, forms delicate white or colourless microscopic needles, only slightly soluble in cold water, and not easily in hot; insoluble in alcohol, ether, and benzene. The water of crystallisation is lost only after some hours' exposure to a temperature close upon 200° C.

Barium Dinaphthyl (ββ)-monosulphonate,

$$\frac{C_{10}H_7.C_{10}H_6.SO_3}{C_{10}H_7.C_{10}H_6.SO_3}>Ba + 2H_2O\ (?).$$

—The barium salt of ββ-dinaphthylmonosulphonic acid was prepared exactly in the same way as in the case of the calcium salt.

The precipitate obtained on cooling the solution was very similar in appearance and solubility to the calcium salt.

A portion was dried at 150° in the air-bath, and the barium in it determined. The results were as follows:—

(I.) Weight of salt taken.... 0·0975 gram
$BaSO_4$ obtained..... 0·0270 „ } = 16·31 p c. Ba.

(II.) Weight of salt taken.... 0·0660 gram
$BaSO_4$ obtained..... 0·0185 „ } = 16·31 p. c. Ba.

	I.	II.	Calculated for $\frac{C_{10}H_7.C_{10}H_6.SO_3}{C_{10}H_7.C_{10}H_6.SO_3}>Ba$.
Ba	16·31 p. c.	16·31 p. c.	15·81 p. c.

Only small yields could be obtained of both calcium and barium salts, other products being formed at the same time as the monosulphonic acid, and apparently with greater facility.

In order to obtain a more highly substituted sulphonic acid than the monosulphonate, 10 grams of the $\beta\beta$-dinaphthyl were heated with an excess of concentrated sulphuric acid (7 grams) in a flask in the oil-bath to a temperature of 180—200° for 5—6 hours. The mass in the flask, on cooling, solidified to a hard shining pitch-like substance. It was boiled with water, neutralised with barium carbonate, filtered in the cold, and the filtrate was evaporated to dryness on the water-bath. A much more soluble product was obtained than in the previous case, in which a smaller amount of sulphuric acid was employed; also by this manner of operating scarcely any monosulphonate could be detected.

By the above-mentioned process two isomeric sulphonic acids appear to be formed, one yielding a barium salt of difficult solubility, the other an easily soluble barium salt. Two similar lead salts are also obtained.

The soluble barium salt presented the appearance of a crystalline powder of a yellowish-white colour. This was heated for several hours in the air-bath to 200°, and in a portion the barium was determined:—

(I.) Substance taken .... 0·1410 gram
BaSO$_4$ obtained .... 0·0600 „ } = 25·02 p. c. Ba.

(II.) Substance taken .... 0·1680 gram
BaSO$_4$ obtained .... 0·0730 „ } = 25·55 p. c. Ba.

	I.	II.	Calculated for $C_{10}H_6.SO_3 \diagdown \atop C_{10}H_6.SO_3 \diagup$ Ba.
Ba	25·02 p. c.	25·55 p. c.	24·97 p. c.

Barium ($\beta\beta$) *Dinaphthyl-disulphonate*, $\begin{matrix} C_{10}H_6.SO_3 \diagdown \\ \vert \qquad\quad \\ C_{10}H_6.SO_3 \diagup \end{matrix}$Ba + xH$_2$O.—

This is the soluble barium disulphonate, the preparation of which has already been described by one of us (*Chem. Soc. J.*, 1877, ii, 557). Its isomeride is a salt soluble with difficulty in water, and not to be confounded with the monosulphonate, which crystallises in microscopic needles, whereas the former falls as a fine white crystalline powder. This soluble disulphonate forms a glassy mass, which readily splits up into lanceolate leaflets. It is insoluble in alcohol, ether, and benzene.

Lead ($\beta\beta$)*Dinaphthyl-disulphonate*, $\left.\begin{matrix}C_{10}H_6.SO_3\\ |\\ C_{10}H_6.SO_3\end{matrix}\right\rangle Pb + xH_2O$.—The soluble lead salt was a light yellowish-white crystalline powder, a portion of which on drying at 200° C. and analysing with reference to the lead in the same way as with the barium salt, gave numbers indicating the formula given.

Lead ($\beta\beta$)*Dinaphthyl-tetrasulphonate*, $\begin{matrix}C_{10}H_5.(SO_3)_2.Pb\\ |\\ C_{10}H_5.(SO_2)_2.Pb\end{matrix} + 6H_2O$.—By employing a slightly larger quantity of sulphuric acid, this time Nordhausen acid, and afterwards neutralising with lead carbonate, the soluble lead salt was obtained of a dinaphthyl-tetrasulphonic acid.

(I.) 0·2260 gram substance gave 0·1290 $PbSO_4$.
0·2400 „ „ 0·0245 H_2O (at 208°).

(II.) 0·5005 gram substance dried in a vacuum over sulphuric acid till the weight became constant, gave 0·2745 gram of lead sulphate.

	I.	II.	Calculated for $\begin{matrix}C_{10}H_5.(SO_3)_2.Pb\\ |\\ C_{10}H_5.(SO_3)_2.Pb\end{matrix} + 6H_2O$.
Pb	38·39	37·46	37·91 p. c.
H_2O.....	10·21	—	9·89 „

This salt was easily soluble in water, but insoluble in alcohol, ether, and benzene.

LXXV.—*On Citraconic and Mesaconic Ethers, and Maleic and Fumaric Acids.*

By W. H. Perkin, F.R.S.

The differences existing between α- and β-coumaric acids have been seen to be comparable with those of maleic and fumaric acids, and also to citraconic and mesaconic acids (*Jour. Chem. Soc.*, 1881, p. 409). Lately a fresh point of resemblance in this direction has been found to exist between the two latter acids by Petri (*Ber.* **14**, 1634), whose researches show that as α-methylcoumaric acid (α-methylorthoxyphenylacrylic acid) when distilled with phosphoric chloride yields the chloride of the β-acid, so citraconic acid or anhydride, under the same circumstances, yields the chloride of mesaconic acid.

There is, however, a considerable divergence found in one of the physical properties of their ethers, viz., in the boiling points, for whereas the ethers of the α-coumaric acid boil at temperatures lower than those of the β-acid, the ethers of maleic and citraconic acids boil at temperatures higher than those of the corresponding fumaric and mesaconic acids.

As boiling points however are not apparently always consistent, sometimes showing a large difference, and at other times a scarcely perceptible one for the same variation in structure, as for example in the case of para- and ortho-toluidine, where there is only 1° between them, and para- and ortho-acetyltoluidine, where there is no less than 10°, it was thought desirable to compare some of the other physical properties, to see if they would follow in the same direction as those of the α- and β-coumaric compounds, or in the opposite, like the boiling points. For this purpose the methylic ethers of citraconic and mesaconic acids were first selected, because it was expected that they would show their physical differences in a more marked manner than the ethylic ethers. As they have not been prepared before, I have given the methods employed for their formation somewhat in detail.

Methylic Citraconate.

Citraconic acid dissolved in methylic alcohol was saturated with hydrochloric acid gas, the mixture being kept cold or nearly so. After standing for about 12 hours, a gentle heat was applied to remove part of the hydrochloric acid. The product was then mixed with ether, washed with water, and then with dilute sodic carbonate. The neutral ethereal solution was dried over anhydrous potassic carbonate and distilled. After the ether had mostly come over, the thermometer quickly rose and became stationary at 208—209°. The product gave on analysis the following numbers:—

0·1201 gram of substance gave 0·3351 gram of CO_2, and 0·072 gram OH_2.

	Theory for $C_7H_{10}O_4$.	Experiment.
Carbon	53·16	53·38
Hydrogen	6·30	6·60

Methylic citraconate distils at 212° with the entire column in the vapour. It is a colourless oil soluble in about 35 parts of water at 15°. Its odour is aromatic and not unpleasant; in taste it is somewhat like oil of aniseed, but not nearly so sweet. It is but little affected by distillation; nevertheless from the analysis given above, which was made of a specimen distilled five or six times, it apparently undergoes slight decomposition, the carbon being a little high.

Its density, determined in a Sprengel U-tube (as were all the others in this paper), was found to be as follows:—

At 15°	1·1168
„ 30	1·1050

compared with water at the same temperatures.

The magnetic rotary power for the yellow ray at 24° was 1·063, water = 1.

Thinking that the methylic citraconate made by this process might contain mesaconate, owing to the action of the hydrochloric acid used, a quantity was prepared from argentic citraconate and methylic iodide; it was found, however, to possess exactly the same boiling point and specific gravity, showing that both processes yield it of equal purity.

Methylic Mesaconate.

This was prepared by saturating a mixture of methylic alcohol and mesaconic acid with hydrochloric, no precaution of cooling being used. It was purified in exactly the same manner as the methylic citraconate. On distillation it mostly came over at 201—202°, and gave on analysis the following numbers. The product used had been frequently distilled.

0·13 gram of substance gave 0·2542 gram CO_2, and 0·0776 gram OH_2.

	Theory for $C_7H_{10}O_4$.	Experiment.
Carbon	53·16	53·32
Hydrogen	6·30	6·63

Methylic mesaconate suffers but little decomposition on distillation; with the entire column of the thermometer in the vapour, it boils at 205°. It dissolves in about 122 parts of water at 15°, and is therefore much less soluble than the citraconate. It specific gravity is—

At 15°	1·1254
„ 30	1·1138

compared with water at same temperatures.

The magnetic rotary power for the yellow ray at 24° is 1·154, water = 1.

Methylic mesaconate was also prepared from mesaconic chloride and methylic alcohol; the product however boiled nearly 5° higher than the foregoing, and contained some chlorine, probably due to a small quantity of some addition product; the chlorine, however, was removed by boiling with the copper-zinc couple. Nevertheless its

boiling point changed but little; its density was higher than that given above. These differences are probably due to some impurity.

Ethylic Citraconate.

This was prepared in the same manner as the methylic compound, but using ethylic alcohol. It boiled at 226°, but with the whole column in the vapour, at 231·75°, a number nearly identical with that observed by Petri, viz., 231° (*Ber.*, **14**, 1634).

Its density was found to be—

At 15°	1·051
„ 30	1·038

compared with water at the same temperatures.

Its magnetic rotary power for the yellow ray at 24° was 1·120, water = 1.

Ethylic Mesaconate.

Prepared in a similar manner to the above, it boiled at 223—223·5°, with the whole column in vapour, at 229°. This boiling point is identical with that obtained by Petri.

Its density was found to be—

At 15°	1·051
„ 30	1·039

The rate of expansion of ethylic mesaconate being rather greater than the ethylic citraconate at 45°, their densities become almost identical.

The magnetic rotary power for the yellow ray at 25° was 1·168, water = 1.

From the examination of the above ethers, we find that the boiling points of the methylic ethers are more widely apart than those of the ethylic.*

Methylic citraconate	212°
„ mesaconate	205
	7 diff.

		Petri.
Ethylic citraconate.....	231·75°	231°
„ mesaconate	229·00	229
	2·75	2 diff.

* This is also the case with the fumaric and maleic ethers (Anschütz, *Ber.*, **12**, 2281).

In this particular they correspond with the α- and β-methylic and ethylic methylorthoxyphenyl acrylates, but the variation between each pair of ethers, as previously stated, goes in the reverse direction, the citraconate being the higher of the two.

In the case of the specific gravities and magnetic rotary power, however, we find the mesaconate always the higher.

	Sp. gr.	Diff.	Magnetic rotary power.	Diff.
Methylic citraconate	1·1168	0·0086	1·064	0·09
„ mesaconate	1·1254		1·154	
Ethylic citraconate	1·0500	0·0010	1·121	0·047
„ mesaconate	1·0510		1·168	

Dr. Gladstone has been kind enough to measure the refractive indices of these bodies, and from his account, which is subjoined, it will be seen that the mesaconates in this particular also always give higher numbers than the citraconates.

"I have examined the two pairs of isomerides you sent me, and find the following indices:—

Compound.	Temp.	μ_A.	μ_D.	μ_H.
Citraconate of methyl	15·5	1·4442	1·4504	1·4721
Mesaconate „	16·0	1·4492	1·4564	1·4813
Citraconate of ethyl	16·5	1·4397	1·4459	1·4659
Mesaconate „	16·0	1·4433	1·4499	1·4727

"The following are the refraction equivalents for A and H:—

Compound.	A.	H.	Dispersion equivalent.
Citraconate of methyl	62·87	66·82	3·95
Mesaconate „	63·10	67·62	4·52
Citraconate of ethyl	78·04	82·69	4·65
Mesaconate „	78·53	83·74	5·21

"It would appear from these that the refractions of the two isomerides are very nearly the same for the beginning of the spectrum, but in each instance the mesaconate appears distinctly more dispersive.

"On the supposition that C = 5·0, H = 1·3, and O = 2·9, the refraction equivalent of the methyl compounds should be 59·6, and that of

the ethyl compounds 74·8. The experimental results are more than three above these figures, but Brühl would probably reckon a part at least of the O at 3·4, and consider that two of the carbon-atoms have the higher value of 6·1, as in such bodies as amylene and the allyl compounds."

We thus see that, except in the boiling points, all the physical properties as yet examined of these isomeric ethers, are consistent in direction with those of the α- and β-coumaric ethers.

Many attempts have been made to obtain an anhydride from fumaric acid other than maleic anhydride, which is produced by its distillation, and therefore at a high temperature. Although thinking that fumaric and maleic acids had but one anhydride common to them, I have made some experiments in this direction, and obtained the following results.

The first experiment was made with an ethereal solution of fumaric chloride and silver oxalate, theoretical quantities being used.

The mixture gradually gave off carbonic anhydride and carbonic oxide, but after standing for six or seven days, not one-tenth part of the amount of gas required by theory had been evolved; the reaction then appeared to stop. The same experiment made in a sealed tube heated to 100°, did not yield a more promising result. In fact, the chloride had apparently entered into direct combination with the silver salt, dry ether dissolving out scarcely anything from the product.

Fumaric chloride dissolved in pure benzene was then brought in contact with argentic fumarate, and the benzene distilled off slowly in the water-bath, a certain amount of decomposition took place, and the dry residue when extracted with petroleum spirit gave a solution which on cooling deposited crystals of maleic anhydride. The amount obtained was very small in comparison with the materials used, most of the product being an insoluble compound apparently of the chloride and silver salt.

Fumaric chloride in the pure state was brought in contact with argentic fumarate, a powerful reaction set in, with evolution of much heat, and maleic anhydride was produced in quantity.

A solution of fumaric chloride in petroleum spirit was added to the theoretical quantity of dry silver carbonate, some carbonic anhydride was given off, and on boiling the mixture and filtering off the petroleum, the solvent on standing gave beautiful crystals of maleic anhydride, the amount however was very small.

It has been stated that acetylic chloride is without action upon fumaric acid (Anschütz, *Ber.*, **10**, 1881). As, however, it appeared probable that the temperatures previously used had not been above

the boiling point of acetylic chloride, experiments were made with these substances in sealed tubes.

In the first experiment the heat was raised quickly until it reached 190—194°; at this temperature the fumaric acid rapidly disappeared, and on distilling the product maleic anhydride was obtained in quantity. As the change took place so readily in this case, it was thought that it might probably be effected at a lower temperature: a mixture of these substances was therefore heated to 100° in a sealed tube. After a few hours' digestion, it was noticed that the fumaric acid began to disappear, and in the course of 24 hours the tube contained a clear solution consisting of maleic anhydride dissolved in acetic acid and acetyl chloride. Hydrochloric acid was also present in quantity and escaped on opening the tube.

This experiment was repeated with some freshly prepared acetyl chloride, but it was found that little or no action took place. It therefore appeared probable that there had been acetic acid in the chloride previously used, especially as it had been made several months. A mixture of acetylic chloride with 25 per cent. of glacial acetic acid was therefore sealed up with fumaric acid and heated in the water-bath. In this case the fumaric acid gradually disappeared, and in the course of 14 hours the contents of the tube was a clear fluid. This on examination was found to contain maleic anhydride in quantity. The experiment was also made with a mixture of equal parts of acetyl chloride and glacial acetic acid. The reaction in this case took place more rapidly than in the above.

We thus see from the above that fumaric acid yields at temperatures not exceeding 100° maleic anhydride, both from its chloride and silver salts, and also when dehydrated with acetyl chloride in presence of acetic acid.

From all the evidence we have, it now appears that we have arrived at the remarkable fact that there is but one anhydride for maleic and fumaric acids, one anhydride for citraconic and mesaconic acids, and one anhydride for α- and β-coumaric acids.

To what, then, can the isomerism of these acids be due, unless it is to a difference in the relationship of the hydroxyl to the radicals?

The physical properties of the ethers are consistent (boiling points excepted), showing that in the conversion of maleic, citraconic, and α-coumaric acids into their isomerides, contraction takes place, and therefore a greater compactness in the molecules results. The effect of this, as might have been expected, is greater stability and diminished solubility.

A comparison of the properties of the aniline salts of some of these isomeric acids has been made, and has given interesting results.

It is well known that a solution of aniline citraconate, when eva-

porated on the water-bath, yields phenylcitraconimide, this change even taking place on keeping a solution of that salt in the cold for some time.

On evaporating a solution of aniline mesaconate to dryness on the water-bath, no similar change takes place, the product remaining perfectly soluble in water.

Fumarate of aniline also remains perfectly soluble after its solution has been evaporated to dryness on the water-bath.

A solution of aniline maleate, however, if evaporated to dryness and kept on the water-bath for some time, becomes mostly insoluble in water, yielding a product which crystallises from alcohol in small brilliant needles, melting at about 210—211°. It is apparently a body analogous to phenylcitraconimide.

A strong solution of aniline maleate, if kept for some time in the cold, deposits a crystalline body; it is, however, different from the above, and dissolves in boiling water.

We see from these observations that the hydroxyls in citraconic and maleic acids are more easily exchanged for another group than those in mesaconic and fumaric acids.

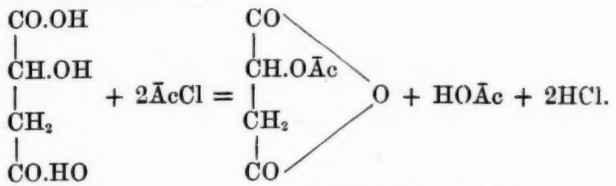
Preparation of Maleic Anhydride from Malic Acid Direct.

In preparing this anhydride, it is usual first to convert malic acid into maleic acid, and dehydrate this, either by repeated distillations, or by treatment with acetyl chloride, as proposed by Anschütz (*Ber.*, **12**, 2281) who succeeded in this way in obtaining 200 grams of maleic anhydride from 1,000 grams of malic acid.

In the decomposition of malic acid by heat, maleic acid appears to be the primary product, fumaric acid being formed afterwards, and interfering greatly with the yield of the maleic acid.

This being the case, it was thought probable that, if malic acid could be converted into an anhydride, which could not give off water when decomposed by heat, it would probably yield maleic anhydride only, and thus the formation of fumaric acid might be avoided.

Such a derivative of malic acid was likely to be produced by the action of acetyl chloride, it being probable that an acetomalic anhydride would be formed thus:—

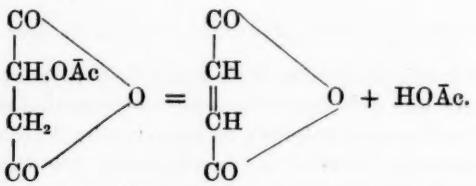


Malic acid. Acetomalic anhydride.

A quantity of malic acid was therefore treated with an excess of acetylic chloride; a reaction soon set in, hydrochloric acid being abundantly given off. When the evolution of this gas had slackened, the mixture was heated in a water-bath, and it soon became a transparent, somewhat gummy fluid. This product has not been examined, but there can be but little doubt that it consisted chiefly of acetomalic anhydride. It was distilled; at first the excess of acetylic chloride came over, then acetic acid. When the temperature had risen to about 160°, the receiver was changed, and all the remaining product collected in it. A small quantity of a carbonaceous residue was left in the retort.

The high-boiling product was redistilled, and after the temperature had reached about 192°, the distillate was collected separately. It all came over under 198° as a colourless oil, which became a perfectly hard, crystalline mass on cooling, and was practically pure *maleic anhydride;* by fractioning the product boiling below 192° a small quantity more was obtained.

The formation of this anhydride from acetomalic anhydride is easily explained thus:—



No fumaric acid is formed by this process if the malic acid has been *thoroughly* treated with acetylic chloride.

The yield obtained is large, but as the malic acid employed was in a damp condition, the percentage cannot be well estimated. The lowest yield obtained from this acid was 40 per cent., the highest 48 per cent. No doubt still larger proportions may be obtained.

Maleic anhydride, when distilled with phosphoric chloride, yields, as was expected, fumaric chloride. It is not quickly acted upon by this reagent, and a good deal of unchanged anhydride distils over at the end of the operation.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY,

SESSION 1880–81.

November 4th, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On the Compounds of Vanadium and Sulphur:" by E. W. E. Kay.

"On the Atmospheric Oxidation of Phosphorus, and some Reactions of Ozone and Peroxide of Hydrogen": by C. T. Kingzett.

"On the Action of Zinc-ethyl on Benzoylic Cyanide:" by E. Frankland and C. C. Graham.

"On Bismuth and Bismuth Compounds:" by M. M. P. Muir, G. B. Hofmeister, and C. E. Robbs.

"On the Colour Properties and Relations of the Metals Copper, Nickel, Cobalt, Iron, Manganese, and Chromium:" by T. Bayley.

"On the Action of Diazonaphthalene on Salicylic Acid:" by P. F. Frankland.

"On the Basic Sulphates of Iron:" by Spencer Pickering.

"Fourth Report on Researches in Chemical Dynamics:" by C. R. A. Wright, E. H. Rennie, and A. E. Menke.

"On some Naphthalene Derivatives:" by H. E. Armstrong and N. C. Graham.

"On the Manufacture of Caustic Soda from the Sulphate:" by Messrs. Bevan and Cross.

November 18th, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"Notes on the Oxides of Manganese:" by Spencer Pickering.

"On Aluminium Alcohols (Part I): their Preparation by Means of the Aluminium Iodine Reaction:" by J. H. Gladstone and A. Tribe.

"On the Absorption-spectrum of Ozone:" by W. N. Hartley.

"On the Probable Absorption of the Solar Rays by Atmospheric Ozone:" by W. N. Hartley.

"On the Synthetical Production of New Acids of the Pyruvic Series (Part II, Isobutyryl- and Butyryl-formic Acids):" by E. Moritz.

"On the Ancient Alum Well of Harrogate:" by R. H. Davis.

"On Peppermint Camphor:" by M. Moriya.

"A Short Account of Baeyer's Process for the Artificial Formation of Indigo:" by W. H. Perkin.

December 2nd, 1880.

Dr. Gilbert, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

J. O. Arnold, Sheffield; A. E. Barclay, Bangor, Maine, U.S.; J. K. Crow, Chesterfield; A. G. Chamberlain, Rugby; A. C. Cockburn, South Kensington; P. H. Cathcart, Oakley Square, N.W.; P. F. Frankland, Princes Square, W.; A. E. Garrod, Harley Street, W.; A. E. Hawkes, Liverpool; R. Holliday, Huddersfield; A. Jesseman, Dulwich Old College; W. B. Mason, Bolton; J. A. Macfarlane, Spain; H. A. Mott, New York; R. T. Plimpton, Clapham, S.W.; C. H. Sharples, Preston; F. M. Sexton, Burslem; B. H. Thwaite, Bolton; J. H. Thompson, Auckland, New Zealand; J. M. Wybord, Bromley, Kent; T. Farrington, Cork.

The following papers were read:—

"On the Volumes of Sodium and Bromine at their Boiling Points:" by W. Ramsay.

"On the Volume of Phosphorus at its Boiling Point:" by D. O. Masson and W. Ramsay.

"On the Specific Volume of Chloral:" by Laura Maude Passavant.

"Note on the Formation of Carbon Tetrabromide in the Manufacture of Bromine:" by J. C. Hamilton.

"Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra:" by W. N. Hartley.

December 16th, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On the Estimation of Nitrogen by Combustion, including Nitro-compounds:" by J. Ruffle.

"On some Naphthalene Derivatives:" by H. E. Armstrong and N. C. Graham.

"On the Effects of Pressure on some Fusing Points:" by T. Carnelley.

January 20th, 1881.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On Pentathionic Acid:" by V. Lewes.

"A Preliminary Note on some Hydrocarbons from Resin Spirit:" by H. E. Armstrong.

"On the Determination of the Relative Weight of Single Molecules:" by Dr. Vogel, of San Francisco.

"On the Synthetical Production of Ammonia by the Combination of Hydrogen and Nitrogen in Presence of Heated Spongy Platinum:" by G. S. Johnson.

"On the Oxidation of Organic Matter in Water:" by A. Downes.

"Analysis of Queensland Soils:" by A. Liversidge.

"On the Volumes of some Compounds of the Benzene, Naphthalene, Anthracene, and Phenanthrene Series:" by W. Ramsay.

"On a New Theory of the Conversion of Bar Iron into Steel by the Cementation Process:" by R. Marsden.

"On the Action of Sulphydrate of Potassium on Chloral Hydrate:" by W. W. J. Nicol.

February 3rd, 1881.

Dr. Gladstone, Vice-President, in the Chair.

The following papers were read:—

"On the Estimation of Organic Carbon in Air:" by A. Dupré and H. W. Hake.

"On the Action of Copper-Zinc Couple upon Nitrates, and the Estimation of Nitric Acid in Water Analysis:" by M. W. Williams.

"On the Position taken by the Nitro-group on Nitrating the Dibromotoluenes:" by R. Nevile and A. Winther.

"On some of the Various Derivatives of Toluene and the Toluidines:" by R. Nevile and A. Winther.

February 17th, 1881.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

B. Akroyd, Elland; M. M. Bird, Blandford; W. E. Benton, Leicestershire; H. Baker, Manchester; M. Benjamin, New York; H. P. Cooper, Highbury, N.; W. H. Coffin, South Kensington; J. J. Eastick, Lewisham, S.E.; H. W. Fenner, Beckton; M. P. Gossett, Portslade, Sussex; S. Harvey, Canterbury; J. W. James, Bristol; T. H. Judson, Llandovery; A. J. King, Withington, Manchester; W. E. Kay, Farnworth; C. A. McMunn, Wolverhampton; W. G. McMillan, Jermyn Street, W.; W. J. Stavert, New College, Oxford; T. Takamatsu, Tokio, Japan; P. Vieth, Bayswater; G. J. Wishart, Edinburgh; R. W. Walker, Lancashire.

The following papers were read:—

"On the Estimation of Organic Carbon in Water-Analysis, Simultaneously with the Estimation of Nitric Acid:" by M. W. Williams.

"On the Influence of the Molecular Grouping in Organic Bodies on the Absorption in the Infra-red Region of the Spectrum:" by Capt. Abney and Col. Festing.

"On the Absorption-bands in the Visible Spectrum produced by Certain Colourless Liquids:" by J. W. Russell and W. Lapraik.

"On the Action of Hydrochloric Acid on Ethylene Alcohol:" by C. Schorlemmer.

"On an Attempt to Accelerate the Process of Determining the Soluble Salts in a Soil:" by E. W. Prevost.

March 3rd, 1881.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On the Action of Bacteria on Various Gases:" by F. Hatton.

"On the Influence of Intermittent Filtration through Sand and

Spongy Iron on Animal and Vegetable Matters Dissolved in Water, and on the Reduction of Nitrates by Sewage:" by F. Hatton.

"On River Water:" by C. M. Tidy.

"On β-Diquinoline:" by F. R. Japp and C. Colborne Graham.

March 17th, 1881.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

W. E. Adeney, Royal College of Science, Dublin; H. Borns, Brompton; J. F. Braga, India; T. C. Day, Burton-on-Trent; R. A. Edgell, Shrewsbury; E. G. Gill, King Henry's Road, N.W.; M. Hiddingh, Cape of Good Hope; P. B. Mills, Chigwell, Essex; O. V. Pisani, Kennington; L. T. O'Shea, Sheffield; F. Tiemann, Berlin; G. Valentine, Arbroath, N.B.; A. Walker, Glasgow.

The following papers were read:—

"On the Volume of Mixed Liquids:" by T. D. Brown.

"On the Action of Alcohol on Mercuric Nitrate:" by R. Cowper.

"On Boron Hydride:" by F. Jones and R. L. Taylor.

"On the Action of Aldehydes on Phenanthraquinone in Presence of Ammonia:" by F. R. Japp and E. Wilcock.

"On the Action of Benzoic Acid on Naphthaquinone:" by F. R. Japp and N. H. J. Miller.

"Note on the Appearance of Nitrous Acid during the Evaporation of Water:" by R. Warington.

"On the Sweet Principle of *Smilax glycophylla*:" by C. R. A. Wright and E. Rennie.

"Note on Usnic Acid and some Products of its Decomposition:" by the late J. Stenhouse and C. E. Groves.

"On the Absorption of Solar Rays by Atmospheric Ozone, and on the Blue Tint of the Atmosphere:" by W. N. Hartley.

"On the Nature of Certain Volatile Products contained in Crude Coal Tar Benzenes:" by Watson Smith.

"On New Zealand Kauri Gum:" by E. H. Rennie.

March 30th. (Annual General Meeting.) See page 177.

April 7th, 1881.

Dr. Russell, Treasurer, in the Chair.

The following papers were read:—

"On the Organic Matter in Sea Water:" by W. Jago.

"On the Action of Compounds Inimical to Bacterial Life:" by W. M. Hamlet.

April 21st, 1881.

Dr. Debus in the Chair.

The following papers were read:—

"On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride:" by F. D. Brown.

"On the Estimation of Hydrogen Peroxide by Means of Potassic Permanganate:" by W. E. Adeney.

"On the Oxidation of Sulphurous Acid:" by H. B. Dixon.

"On the Reduction of Cinnylic Alcohol:" by F. Hatton and W. R. Hodgkinson.

May 5th, 1881.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

A. J. Anderson, Clapham, S.W.; F. J. O'Farroll, Dublin; T. R. Ord, Holloway, N.; G. C. Robinson, Hull; A. J. Shilton, Birmingham; W. R. Smith, Cheltenham; F. P. Venable, North Carolina, U.S.A.; G. H. With, Hereford.

The following papers were read:—

"On the Action of Humic Acid upon Atmospheric Nitrogen:" by by E. W. Prevost.

"On the Active and Inactive Amylamines:" by R. T. Plimpton.

"On the Action of Sodium Alcoholates on Fumaric Ethers:" by T. Purdie.

"On the Products of the Action of Alkalis on Ethylic β-Ethylacetosuccinate:" by L. T. Thorne.

"On some Carbazol Compounds:" by E. H. Rennie and W. R. Hodgkinson.

May 19th, 1881.

Prof. Roscoe, President, in the Chair.

The following papers were read:—

"On Ammonium Nitrite, and the Reaction between Hydrogen and Nitric Oxide in Presence of Spongy Platinum:" by L. T. Wright.

"On the Synthetical Production of Urea from Benzene, Ammonia, and Air, by the Action of Heated Platinum:" by E. F. Herroun.

"On a proposed Volumetric Method for the ready estimation of a Soluble Sulphite and free Sulphurous Acid, or of free Sulphurous and Sulphuric Acids, even in presence of Sulphates:" by O. V. Pisani.

"On the Identification of Crystallised Alkaloïds, &c., by the Microscope and the use of Polarised Light:" by A. Percy Smith.

"On the Colour-properties and Colour-reactions of the Metals of the Iron Copper-group:" by T. Bayley.

"On the Effects of the Growth of Plants on the amount of matter removed from the Soil by Rain:" by E. W. Prevost.

"On the Action of Sodium on Cinnamic Ether:" by F. Hatton.

June 2nd, 1881.

Prof. Roscoe, President, in the Chair.

The following papers were read:—

"Experimental Researches on the Amalgamation of Silver Ores:" by C. Rammelsberg.

"On the Action of Solvents on Saponified Oils and Waxes:" by A. H. Allen and W. Thomsen.

"On the Sulphides of Copper, and a Determination of their Molecular Weight:" by S. U. Pickering.

"Chemical Examination of the Buxton Thermal Water:" by J. C. Thresh.

"On Potable Waters, Part II. Determination of Total Solids:" by E. J. Mills.

"On the Estimation of the Value of Zinc-powder, and on a Gauge for Measuring the Volume of Gases without Calculation for Temperature and Pressure:" by J. Barnes.

June 16th, 1881.

Prof. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

A. E. Davies, Halton, near Runcorn; A. B. Avarne, Canonbury, N.; G. H. Bostock, Manchester; W. Bedford, Workington; B. Browning, Rotherhithe; J. M. Collett, Gloucester; J. E. Doyle, Birmingham; A. W. Duncan, Manchester; H. Frankland, Middlesbro'; A. J. Hailes, Hornsey, N.; C. W. Marsh, New Jersey, U.S.; A. Philip, St. John's, S.E.; T. K. Rodgers, Madras; J. Schwartz, Highbury, N.; O. Trigger, Camden Square, N.W.; G. Tate, Liverpool; J. P. Wilkes, Abchurch Lane, E.C.

The following papers were read:—

"On the Isomeric Acids obtained from Coumarin, and the Ethers of Salicylaldehyde:" by W. H. Perkin.

"Notes on Naphthalene Derivatives:" by H. E. Armstrong and G. Lowe.

"On the Synthesis of Ammonia:" by G. S. Johnson.

"On the Alkaloïds of Nux Vomica:" by W. A. Shenstone.

"Notes on Photographs of the Ultra-Violet Emission-spectra of certain Elements:" by W. N. Hartley.

"On the Sulphates of Aluminium:" by S. U. Pickering.

"On two new Oxides of Bismuth:" by M. M. P. Muir.

Donations to the Library, 1880–81:—

"Introduction to the Study of Chemical Philosophy:" by Dr. W. A. Tilden: from the Author.

"Introduction to the Study of Organic Chemistry:" by Dr. H. E. Armstrong: from the Author.

"Practical Organic Chemistry:" by H. Chapman Jones: from the Author.

"Researches on Thermometry:" by Dr. E. J. Mills: from the Author.

"Historical Sketch of the Progress of Pharmacy in Great Britain:" by Theophilus Redwood: from the Pharmaceutical Society.

"The Wild Silks of India, principally Tussor:" by Thomas Wardle: from the Author.

"The Norwegian North Atlantic Expedition:"

1. "On the Air in Sea-water:"
2. "On the Carbonic Acid in Sea-water:"
3. "On the Amount of Salt in the Water of the Norwegian Sea:" by Hercules Tornböe: from the Author.

"Bulletin of the United States Geological and Geographical Surveys of the Territories." Vols. 4 and 5, 1878—1880.

"Geological and Geographical Survey of the Territories of Idaho and Wyoming:" by F. V. Haydon.

"Lands of the Arid Region of the United States:" by J. W. Powell.

"History of North American Pinnipeds: Monograph of the Walruses, Sea-lions, Sea-bears, and Seals of North America:" by Joel Asaph Allen: from the Department of the Interior, United States.

Pamphlets:—

"The Dynamo-Electric Current:" by Dr. C. W. Siemens: from the Author.

"Gas and Electricity as Heating Agents:" by Dr. C. W. Siemens: from the Author.

"The Melbourne Water Supply:" by Sydney Gibbons: from the Author.

"Report of the Results of Experiments made with samples of Dust collected at Seaham Colliery:" by F. A. Abel: from the Author.

"Note on the Occurrence of Recent Plants in Brown Iron Ore:" by J. Arthur Phillips: from the Author.

"On the Constitution and History of Grits and Sandstones:" by J. Arthur Phillips: from the Author.

"Physiology of Every-day Life:" by J. F. M. Harris Stone: from the Author.

"Letter to the Commissioner of Agriculture (U.S.) on Sorghum Sugar:" by J. W. Johnston: from the Author.

"Résumé of Progress in Agricultural Science in the United States in 1878:" by W. O. Atwater: from the Author.

"Glace sous la Pression Critique:" par A. Boutlerow: from the Author.

Periodicals:—

"Philosophical Transactions for 1880:" from the Royal Society.

"Transactions of the Royal Society of Edinburgh." Vol. xxix, Part II (1879–80).

Proceedings of the same (1879–80): from the Society.

"Proceedings of the Royal Institution of Great Britain." Vol. ix, Part 3: from the Royal Institution.

"Transactions of the Cambridge Philosophical Society." Vol. ix, Part 1: from the Society.

"Proceedings of the same." Vol. iii, Parts 7, 8; and Vol. iv, Part 1.

"Memoirs and Proceedings of Literary and Philosophical Society of Manchester, 1879:" from the Society.

"Memoirs of the Royal Astronomical Society." Vol. xliv (1879–80): from the Society.

"Calendar of the Mason Science College, Birmingham" (1880–81): from the College.

"Calendar of the Pharmaceutical Society for 1881:" from the Society.

"Pharmaceutical Journal and Transactions, 1880–81:" from the Society.

"Year-book of Pharmacy, 1880:" from Professor Attfield.

"Journal of the Iron and Steel Institute, 1881:" from the Institute.

"Proceedings of the Physical Society of London." Vol. iv, 1881: from the Society.

"Report of the British Association for the Advancement of Science, for 1880:" from the Association.

"The Chemical News, 1880–81:" from the Editor.

"Journal of the Society of Arts, 1880-81:" from the Society.

"The Analyst for 1881:" from the Editors.

"The Chemist and Druggist, 1881:" from the Editor.

"Quarterly Journal of Science." Vol. xi: from the Editor.

"Quarterly Journal of the Geological Society, 1881:" from the Society.

"Proceedings of the Literary and Philosophical Society of Liverpool, 1879–80:" from the Society.

"Proceedings of the Royal Society of Glasgow, 1879–80:" from the Society.

"Transactions of the Royal Irish Academy, 1880:" from the Academy.

"Journal and Proceedings of the Royal Society of New South Wales." Edited by Prof. Liversidge, 1880. Vol. xiv: from the Editor.

"The American Chemical Journal:" edited by Prof. Ira Remsen. Vol. i, ii, and iii (1879–81): from the Editor.

"American Journal of Science and Arts." Vols. xxi and xxii: from the Editors.

"Journal of the Frankland Institute, 1881:" from the Institute.

"Proceedings of the Academy of Natural Sciences at Philadelphia, 1880:" from the Academy.

"Memoirs and Proceedings of the Literary and Philosophical Society of Manchester, 1879:" from the Society.

"Boletin de la Academia Nacional de Ciencias de la Republica Argentina, 1879:" Nos. 2 and 3: from the Academy.

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